ELEMENTS OF CHEMISTRY.

LONDON:
SAVILL AND EDWARDS, PRINTERS, CHANDOS STREET,
COVENT GARDEN.

ELEMENTS OF CHEMISTRY:

THEORETICAL AND PRACTICAL.

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SANCTE ET SAPIENTER

PART II.

INORGANIC CHEMISTRY.

SECOND EDITION, WITH ADDITIONS.

LONDON:
JOHN W. PARKER AND SON, WEST STRAND.
1860.

LONDON:
SAVILL AND EDWARDS, PRINTERS, CHANDOS STREET,
COVENT GARDEN.

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PART II.

INORGANIC CHEMISTRY.

CHAPTER I.

NOMENCLATURE—CLASSIFICATION OF THE ELEMENTS.

(281) *Principles of Chemical Nomenclature.*—Before proceeding to a description of the chemical properties of the different elementary substances, and of the compounds which are the result of their union with each other, it will be needful to explain the principles upon which the nomenclature in use amongst chemists has been founded. The object of the inventors of this language was, not merely to give a distinguishing name to the substances spoken of, but also to convey a knowledge of their components, and even of the proportions in which those components occur. In the less complicated substances with which the chemist has to deal, this object is very completely attained. In those of a more complex nature, the employment of symbols (15) becomes necessary, in order to enable the composition of the body to be fully indicated, and the *formula* of a substance, especially if the substance be derived from the animal or the vegetable kingdom, becomes a necessary supplement to its name.

1. *Elements.*—In the case of the elementary bodies, the common name of each is usually that by which it is distinguished in chemical language, if the substance—as is the case with many of the metals, such as lead, iron, copper, or zinc—be one which is familiarly known: if it be a body which the researches of the chemist have brought to light, the name is generally indicative of some marked peculiarity by which the element is characterized. Thus phosphorus ('the light bearer') is so named because when exposed to the air it emits a feeble light which is visible in a darkened room; iodine derives its name from the violet colour of its vapour; hydrogen ('producer of water'), from the circumstance that it is a necessary component of water; and so on.

The attempt to introduce a strictly systematic nomenclature for the elementary substances has failed, owing to the strong hold which the popular names of those in familiar use have retained upon the language; but in the case of the more recently discovered metals a common termination in *um* has been assigned to them, as, for example, palladium, iridium, osmium, potassium, sodium, aluminum, &c. Among the non-metallic elements analogies are also pointed out by a similarity in the termination of the name: thus, chlorine, iodine, bromine, and fluorine, have similar properties; and the existence of a certain analogy between boron and silicon is indicated by the common termination of both.

2. *Binary Compounds.*—When elements combine with each other to form a binary compound,—that is to say, a compound in which two elements only are present, and in which also one atomic proportion or equivalent* (11) only of each substance is concerned,—the nature of both the components is specified by the name employed; the name of the electro-negative ingredient (229), being that which is placed first as the generic term, whilst that of the electro-positive or *basylous* element follows as indicating the species: for instance, a combination of oxygen with zinc is designated oxide of zinc—the electro-negative element oxygen standing first and undergoing a modification or inflection in its name. The following table will illustrate the manner in which such modifications are applied; the symbols of the different compounds are given in the fourth column. It is to be observed that in employing symbols the rule observed as to the order in which the elements are arranged is the reverse of that which is adopted in the application of the name, for in the symbol the basylous or electro-positive element is always placed first:—

The compounds of	are termed	For Example:—	Or in symbols
Oxygen	Oxides	Oxide of zinc	Zn O
Chlorine	Chlorides	Chloride of silver	Ag Cl
Bromine	Bromides	Bromide of sodium	Na Br
Iodine	Iodides	Iodide of potassium	K I
Fluorine	Fluorides	Fluoride of calcium	Ca F
Nitrogen	Nitrides	Nitride of boron	B N
Carbon	Carbides or Carburets	Carbide of iron	Fe_4 C
Sulphur	Sulphides or Sulphurets	Sulphide of copper Sulphuret of lead	Cu S Pb S
Selenium	Selenides or Seleniurets	Selenide of mercury Seleniuret of cadmium	Hg Se Cd Se
Phosphorus	Phosphides or Phosphurets	Phosphide of hydrogen Phosphuret of calcium	H P_2 Ca_2 P

* The term *equivalent* has hitherto been very generally employed by chemists

3. *Multiple Compounds.*—It often happens, however, in consequence of the operation of the law of multiple proportions (10), that the same pair of elements forms two or more compounds endowed with different properties, and which contain different proportions of their components: the electro-negative element in this case is usually the one in which the multiple relation is observed; and the number of atoms in which it enters into combination in the particular case is indicated by prefixing to the name an abbreviation of the corresponding Greek ordinal: πρῶτος first, δεύτερος second, τρίτος third, &c. For example, there are four different oxides of osmium:—

The first or lowest oxide is termed the		protoxide of osmium, or, simply, oxide of osmium	$Os\,O$
The second oxide	„	deutoxide of osmium . .	$Os\,O_2$
The third oxide	„	tritoxide of osmium . .	$Os\,O_3$
The fourth oxide	„	tessaroxide, or peroxide of osmium	$Os\,O_4$

Sometimes the Latin prefixes are substituted for those derived from the Greek: thus the terms *bin*oxide and *deut*oxide of nitrogen are used indifferently for a combination (NO_2) of one proportional or atom of nitrogen and two atoms of oxygen. In the same way the *ter*chloride of antimony ($Sb\,Cl_3$) is used as synonymous with the *trito*chloride of antimony. The highest oxide, chloride, or sulphide, is frequently termed the *per*oxide, *per*chloride, or *per*sulphide. Thus the compound $Sb\,Cl_5$ is termed the perchloride of antimony: $Ca\,S_5$ is termed indifferently the persulphide or the pentasulphide of calcium. This practice of using indifferently a

as synonymous with *combining proportion*, or *atomic weight*, and so long as its use is restricted to this sense, it may be so employed without danger of introducing inaccuracy into the reasonings founded upon it.

Laurent, however, in his "Chemical Method," has strongly and justly drawn attention to the essential difference between the significations of the two terms. For example, an acid like the citric ($C_{12}H_5O_{11}$) will require three times as much potash to form with it a neutral salt, as is required by another acid, such as the nitric (NO_5). The proportion of citric acid represented by the formula $C_{12}H_5O_{11}$, is nevertheless frequently termed its *equivalent*, and the same term is also applied to the proportion of nitric acid represented by the formula NO_5; yet it is manifest that these quantities of the two acids are not really equivalent to each other, inasmuch as one of them neutralizes three times as much potash as the other.

In order, therefore, to avoid this solecism, and at the same time to secure brevity in our descriptions, it will be convenient to speak of the quantities of each acid above cited as an *atom* instead of an *equivalent* of their respective acids; a term warranted by the fact that the formula of each represents the simplest expression in symbols which can be adopted to indicate the smallest particle or atom of the compound: the term atom will therefore generally be employed in this work as synonymous with the combining proportion of the compounds to which it refers. Of course the use of the terms *atom* and *atomic weight* implies the admission of Dalton's theory of the atomic constitution of matter.

Greek or a Latin prefix in the names of compounds belonging to the same series is etymologically reprehensible. If, for instance, the compound of tin (SnS) be termed the *protosulphide*, the compound (SnS_2) should, in order to preserve consistency, be termed the *deutosulphide*; but in this case the use of the name *bisulphide* is so generally sanctioned by custom, that the employment of the term deutosulphide in its stead would have a pedantic appearance.

4. *Acids.*—If the oxides possess acid characters, as, for example, is the case with some of the higher oxides of nitrogen, a different plan is adopted to mark this important peculiarity. At the time that the nomenclature was devised by Lavoisier and his coadjutors, oxygen was considered to be the element upon which the existence of the acid character mainly depended, as indeed its name (signifying 'generator of acids') implies. The system of nomenclature was therefore specially adapted to this idea. It frequently happens that an element forms more than one acid with oxygen: the compound which contains the largest proportion of oxygen is in this case indicated by making the name terminate in the syllable *ic*. Nitric acid (NO_5), for instance, is the acid of nitrogen in which the largest quantity of oxygen is found: in like manner sulphuric acid (SO_3) is the most highly oxidized acid of sulphur. A second acid which contains the same elements united with a smaller proportion of oxygen receives a name which ends with the syllable *ous*: thus nitrous acid (NO_3) and sulphurous acid (SO_2) indicate acids in which a smaller proportion of oxygen is present than in nitric and sulphuric acids. When an acid exists in which a still smaller proportion of oxygen is present, the prefix *hypo*— from ὑπο, 'below,' is usually employed; hyposulphurous acid (S_2O_2) is the term employed to designate an acid which contains still less oxygen than sulphurous acid. In a few cases an acid has been discovered which contains still more oxygen than the one to which the termination *ic* had been already appropriated. Chloric acid, for example, is represented as ClO_5, but an acid was subsequently found to exist, which has the composition ClO_7; in this case the prefix *per* (which is an abbreviation for ὑπερ, or *super*, 'above') is employed, the new compound having been termed perchloric acid.*

* The use of the term *acid* involves in some cases a degree of ambiguity, inasmuch as it is applied sometimes to a compound containing hydrogen, and sometimes to a body in which no hydrogen is present. Thus the compound HO, NO_5 is sometimes distinguished as hydrated nitric acid, but it is generally called nitric acid simply, though it is in reality nitrate of oxide of hydrogen, just as KO, NO_5 is nitrate of oxide of potassium: the first being a compound of the anhydrous compound NO_5 and water; the second a compound of the same anhydrous body and potash. Many of the acids may, however, be obtained in an isolated state deprived of water, constituting a class of bodies distinguished as

The progress of research, however, has revealed other acids in which oxygen is wanting, but which are compounds of hydrogen. These acids are usually distinguished by prefixing the word *hydro*, as an abbreviation for hydrogen: thus chlorine and hydrogen form an acid HCl, hydrochloric acid, often called muriatic acid: cyanogen and hydrogen form hydrocyanic or prussic acid, HCy, and so on. Some writers, following the example of Thénard, transpose these terms: they speak of *chlorhydric* acid, and *cyanhydric* acid. There is an advantage in this alteration, since it avoids any ambiguity arising from the use of the prefix *hydro*, which has in some instances been applied to compounds which contain water.

5. *Salts.*—When the acids unite with bases to form salts, the degree of oxidation in the acid is still indicated by the name of the salt. The name of the acid stands first as generic, the name of the base being added to show the species.

When acids ending in *ic* form salts, in naming such compounds the termination of the acid is changed into *ate*: thus the salt formed when nitric acid unites with lime is termed nitrate of lime (CaO,NO_5). When sulphuric acid combines with oxide of iron, the salt is called sulphate of protoxide of iron, or usually, for the sake of brevity, sulphate of iron (FeO, SO_3) : perchloric acid with potash forms the salt called perchlorate of potash (KO, ClO_7). If the name of the acid end in *ous*, the termination is changed to *ite* in naming the salt: thus sulphurous acid and baryta combine and form a salt called sulphite of baryta (BaO, SO_2) : hyposulphurous acid and soda by their union form hyposulphite of soda (NaO, S_2O_2).

It may here be well to caution those who are just commencing the study of chemistry, of the necessity of distinguishing clearly between compounds such as the sulphites and the sulphates, or the sulphides and the sulphites. Sulphide of sodium (NaS) for example, is a binary compound, containing a direct product of the combination of two elementary substances, whereas sulphite of soda

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anhydrides. These anhydrides appear (for reasons which must be discussed hereafter) to contain the elements of the acids in a form different from that in which they exist in their salts. This is the case with nitric acid, which may be procured in a separate form $(NO_5)_2$ as *nitric anhydride*.

In this work the term *acid*, when used without qualification, will be applied to the salts of hydrogen, such as HO, SO_3, sulphuric acid (sulphate of water); HO, NO_5, nitric acid (nitrate of water); HCl, hydrochloric acid, &c. In cases where the substance is in combination with a base, as, for instance, in the nitrate of potash (KO, NO_5), the compound will, notwithstanding, frequently be indicated as consisting of an acid and base, the nitric acid here being $=NO_5$ (the *hemianhydride*); but *in cases of this* description the sense of the term *acid* will be *sufficiently evident from the context*.

(NaO, SO_2) is a more complex compound, formed by the union of two compound bodies with each other. Sulphate of soda (NaO, SO_3), again, contains one proportional more of oxygen than the sulphite of this base.

If more than one equivalent of an acid be united with one equivalent of a base, there is no difficulty in pointing this out in the name. A compound of one equivalent of chromic acid and one of potash (KO, CrO_3) would be spoken of simply as chromate of potash; but there is another compound of potash with chromic acid in which two equivalents of the acid are present to one equivalent of the base; this compound is known as the bichromate of potash ($KO, 2CrO_3$), the circumstance of the additional equivalent of acid being in this and in other analogous cases indicated by the prefix *bi*, from the Latin *bis*, 'twice,' which is made to precede the name appropriated to the neutral salt. The more complicated relation of three equivalents of acid to two of base, or the proportion of 1½ to 1, is expressed by the prefix *sesqui*, which means 'one and a half:' thus the compound of ammonia with carbonic acid, which forms the usual smelling salts, is called sesquicarbonate of ammonia ($2H_4NO, 3CO_2$).

Occasionally it happens that it is the base instead of the acid which increases in multiple proportion. Some of the salts of lead exhibit this mode of combination; in such a case the nature of the compound is indicated by using the prefixes *di* or *dis*, for two equivalents of base, *tri* or *tris*, for three equivalents, and so on; ($2PbO, NO_5$) would be dinitrate of lead, ($3PbO, C_4H_3O_3$) triacetate of lead, &c.

Generally speaking, a metal forms only one salifiable oxide, that is to say, only one oxide which has the power of combining with acids, and thus forming salts: but there are several exceptions to this rule. Iron, for example, may form salts in which the protoxide (FeO) is present. Such salts are commonly distinguished as *protosalts*. ($FeO, SO_3 + HO, 6\ Aq$) represents the composition of the crystallized sulphate of protoxide of iron, and it is often described briefly as protosulphate of iron; but there is another series of salts of iron, in which the peroxide or sesquioxide (Fe_2O_3) of the metal is the base; these are distinguished as the *persalts*, or *sesquisalts*, of iron: ($Fe_2O_3, 3SO_3$) represents the sulphate of the peroxide (or sesquioxide) of iron, and it is usually termed the persulphate, or sesquisulphate of iron. These terms, although in general use, are not free from ambiguity. Berzelius preferred to call the protoxide of iron, *ferrous* oxide, and the protosulphate, ferrous sulphate, whilst the sesquioxide he

termed *ferric* oxide, and the sesquisulphate was upon his plan called ferric sulphate. This form of nomenclature does not assimilate well with our language, but it unites brevity with precision, and may in some cases be employed with advantage.

Other forms of nomenclature are applied in particular cases, but these will be best explained as the examples to which they refer arise.

(282) *Empirical and Rational Formulæ.*—In expressing the composition of a body by the use of symbols, the chemist may either content himself with simply stating the result of analysis by a mere enumeration of the elements and the relative number of proportionals of each; in which case he gives what is termed the *empirical formula* of the body; or he may attempt an explanation of the mode in which he conceives those elements to be associated together, and by the arrangement of his symbols may give expression to a theory of the composition of the body, and thus assign to it a *rational formula*. A body can have but one empirical formula, but it may be represented by a variety of rational formulæ, according to the different views which may be taken as to the mode in which its components are arranged.

Crystallized sulphate of magnesia, for example, has the following empirical formula:—

$$(1)\ MgH_7\ SO_{11}.$$

That is to say, its constituents are present in the ratio of 1 atom of magnesium, 7 atoms of hydrogen, 1 of sulphur, and 11 of oxygen. It is, however, never so written. The water which it contains may be entirely driven off by a heat a little above 400° F.; and it is usually represented as consisting of magnesia, sulphuric acid, and water, as these are the materials out of which it is formed: thus—

$$(2)\ MgO,\ SO_3 + 7\ HO.$$

But it is found that at a heat of 212°, 6 equivalents of the water may be expelled, whilst the 7th equivalent requires a much higher temperature, so that it appears to occupy a position in the salt different from that of the other 6: this fact may be indicated by slightly altering the second formula, as follows:—

$$(3)\ MgO,\ SO_3 + HO,\ 6\ HO.$$

Some chemists, however, guided partly by the results of the electrolysis of the salt, suppose that when once an acid and a base have united, their elements are arranged in an order different from that in which they existed when separate, and they prefer to represent the salt accordingly, as

$$(4)\ Mg,\ SO_4 + HO,\ 6\ HO.$$

Whilst, if sulphuric acid be regarded as dibasic, it would be necessary to represent the formula of the salt as

$$(5)\ 2\ Mg,\ S_2O_8 + 2\ HO,\ 12\ HO.$$

Each of the last four formulæ is a rational formula for sulphate of magnesia; and each conveys far more information than the formula No. 1. Each represents a theory founded upon particular modes of decomposition which the salt may be made to experience.

It is impossible that all these formulæ should truly indicate the molecular constitution of the salt, though each may represent the grouping of its component elements under particular circumstances. Rational formulæ are indeed indispensable as the exponents of the theories which guide the chemist in his researches, or which aid him in arranging and interpreting phenomena; but, like the theories which they represent, they are only temporary expedients, and they must consequently always be regarded as such, and must be modified or discarded when they no longer faithfully represent the conditions of our knowledge of the compound which they are employed to indicate.

(283) *General Arrangement of the Elements adopted in this Work.*—The general division of the elementary bodies into non-metallic and metallic has been already pointed out. There is, however, no strict line of demarcation between the non-metallic and the metallic elements.

The bodies which are considered as non-metallic constitute the electro-negative ingredient in the binary combinations which they form with the metals, and are most of them insulators of the voltaic current. Carbon and silicon, however, in certain forms, act as conductors of electricity. The compounds of the non-metallic elements with oxygen generally show but little tendency to unite with acids; on the contrary, the higher oxides of most of them form powerful acids as the result of their combination with oxygen. These acids, except the silicic, are readily soluble in water; and even silicic acid, under certain circumstances, may be obtained in solution.

The metals, on the other hand, are characterized by a peculiar combination of opacity and compactness, which gives them, when polished, a peculiar brilliancy, termed the metallic lustre; they are good conductors of heat and electricity, and most of them, by combination with oxygen, form powerful bases. It is, nevertheless, sometimes difficult to determine whether a body should be regarded as a metal or not. Arsenic has a high metallic lustre; but it is more closely allied to phosphorus than to any other

elementary substance, and both its oxides are endowed with well-marked acid properties. Tellurium, also, exhibits the closest analogy with selenium and with sulphur, but it possesses high lustre, and some conducting power for electricity.

The subdivision of the simple substances into non-metallic and metallic is, however, convenient to the student, and it will therefore be retained in this work. The order in which the different elementary bodies will be treated is not in all cases that which a rigid adherence to analogy would indicate, though this has been adopted, excepting in those instances in which it seemed more advantageous to the student to follow a different course. In most cases we shall first examine the chemical properties which are exhibited by each of the elements in its uncombined form: we shall then study the general nature of its actions upon other elements, and shall afterwards examine the more important compounds into the formation of which it enters.

In describing the properties of the non-metallic elements, it will be found a convenient arrangement to consider first the four elements which enter into the composition of those all-pervading and all-important substances, air and water, and then to pass on to others, classing them together according to the general analogy of their properties. Following this plan, we shall consider first the properties of what may be termed the *atmospheric group* of elements—viz.,

1. Oxygen	3. Hydrogen (and water)
2. Nitrogen (and the atmosphere)	4. Carbon (and carbonic acid).

Having examined some of the more important compounds which these bodies form with each other, we shall describe the well-marked natural group constituting what Berzelius terms the *Halogens*, from the circumstance of their forming with the metals saline compounds resembling common salt—viz.,

5 Chlorine	7 Iodine
6 Bromine	8 Fluorine.

Four combustible elements will be taken next in order—viz.,

9 Sulphur	11 Tellurium
10 Selenium	12 Phosphorus;

and the general survey of the non-metallic elements will be completed with

13 Silicon	14 Boron.

For the convenience of description and of reference, the metals will be arranged in seven groups in the following order. The elements which compose each group generally present some natural resemblance, though, as already stated, the classification does not in all cases bring together those which, in chemical habitudes, are really the most closely allied.

I. *Metals of the Alkalies—3 in number.*

1. Potassium.	2. Sodium.	3. Lithium.

II. *Metals of the Alkaline Earths—4 in number.*

1. Barium.	3. Calcium.
2. Strontium.	4. Magnesium.

III. *Metals of the Earths—10 in number.*

1. Aluminum.	5. Yttrium.	8. Cerium.
2. Glucinum.	6. Erbium.	9. Lanthanum.
3. Zirconium.	7. Terbium.	10. Didymium.
4. Thorinum.		

IV. *Metals more or less analogous to Iron—8 in number.*

1. Zinc.	4. Nickel.	7. Chromium.
2. Cadmium.	5. Uranium.	8. Manganese.
3. Cobalt.	6. Iron.	

V. *Metals which yield Acids—10 in number.*

1. Tin.	5. Molybdenum.	8. Arsenic.
2. Titanium.	6. Vanadium.	9. Antimony.
3. Columbium.	7. Tungsten.	10. Bismuth.
4. Tantalum.		

VI. 2 *Metals.*

1. Copper.	2. Lead.

VII. *Noble Metals—9 in number.*

1. Mercury.	4. Platinum.	7. Ruthenium.
2. Silver.	5. Palladium.	8. Osmium.
3. Gold.	6. Rhodium.	9. Iridium.

If a strictly natural order were to be followed in grouping the elements, it would, however, be necessary to modify the foregoing

arrangement. This will be rendered evident by pointing out the most important natural groups into which the elementary bodies admit of being subdivided. The detailed indication of the points of resemblance between the members composing each group must be deferred until the properties of the group are considered. In many instances these natural relations between the individual elements thus grouped together are very striking, in others they are more obscurely marked, and in the case of the metals of the earths proper, as well as of the noble metals, the natural affinities of these elements with the others are as yet very incompletely known. In the table which follows they are represented in two converging series.

<table>
<tr><td>Fluorine.</td><td colspan="2">Hydrogen.</td></tr>
<tr><td>Chlorine.
Bromine.
Iodine.</td><td colspan="2">Potassium.
Sodium.
Lithium.</td></tr>
<tr><td>Oxygen.</td><td rowspan="2">Barium.
Strontium.
Calcium.</td><td rowspan="2">Silver.
Lead.
Mercury.</td></tr>
<tr><td>Sulphur.
Selenium.
Tellurium.</td></tr>
<tr><td>Nitrogen.</td><td rowspan="2">Magnesium.
Zinc.
Cadmium.</td><td rowspan="2">Copper.
Nickel.
Cobalt.</td></tr>
<tr><td>Phosphorus.
Arsenic.
Antimony.
Bismuth.</td></tr>
<tr><td>Carbon.</td><td colspan="2">Iron.
Chromium.
Manganese.
Uranium.</td></tr>
<tr><td>Boron.</td><td colspan="2">Aluminum.</td></tr>
<tr><td>Silicon.
Titanium.
Tin.
Tantalum.</td><td colspan="2">Molybdenum.
Vanadium.
Tungsten.</td></tr>
</table>

CHAPTER II.

THE ATMOSPHERE. OXYGEN—NITROGEN.

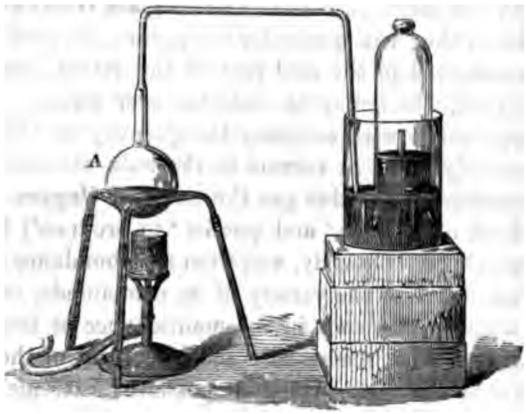
(284) *Compound Nature of the Atmosphere.*—The chemical researches of the philosophers of the last century are especially remarkable on account of the important information which they afforded upon the nature of the atmosphere. Indeed, the knowledge thus obtained may be regarded as the starting point of the brilliant chemical discoveries which have since succeeded each other with such rapidity. These researches have abundantly proved that the air is far from being, as it was once supposed to be, an elementary body. It has been found, on the contrary, to be a mixture of several substances, some of which are elementary, others compound.

The most remarkable and abundant of the constituents of the air are the elementary bodies, oxygen and nitrogen; and of its compound ingredients aqueous vapour and carbonic acid are the most important.

The most direct proofs of the compound character of the atmosphere are afforded by examining the effects produced upon it by burning bodies. Bodies, as is well known, cannot burn without the free access of air. On placing a lighted taper under the receiver of the air-pump and exhausting the air, the flame becomes extinguished. A limited quantity of air will support combustion for but a limited period: a lighted taper floating on water under an inverted bell-glass, the edge of which is plunged beneath the water, soon begins to burn dimly, and at length becomes extinct. But the taper ceases to burn long before the air is all spent; the receiver still contains a large quantity of a gaseous body in which a candle will not burn. The results obtained by burning a candle in a limited portion of air are however rather complicated, because the products which are formed by the burning body rise in the form of gas, and become mixed with the remaining portion of air. Lavoisier contrived to obviate this inconvenience by acting upon the air with a substance which produced a solid body as the result of the chemical action, so that it left the air unmixed with any gas which rose from the burning body. The material which he employed to decompose the air was metallic mercury, a substance which acts very slowly, and which does not burn in the ordinary sense of the term. The experiment may be performed as follows:—

Into the bulb of a flask or retort (A, fig. 242), provided with a

Fig. 242.



neck of considerable length, an ounce or two of metallic mercury is introduced: the neck of the flask is then bent in the manner shown in the figure, and the bent portion plunged into a mercurial bath, so as to leave the open end of the neck projecting above the level of the mercury, into a jar partially filled with atmospheric air. The bulk of this portion of air is then accurately observed, and the temperature and barometric pressure at the time of the observation are recorded. Heat is now applied to the flask, and maintained steadily at a point just below that required to make the mercury boil. If this temperature be continued for three or four consecutive days, the decomposition of the air inclosed both in the flask and in the jar will be effected. The mercury in the flask will gradually become covered with red scales, and the air in the jar, which at first expanded from the action of the heat, will slowly decrease in bulk until fresh scales no longer continue to be formed. When this point is reached the source of heat may be removed, and the remaining air, when cold, will be found to measure nearly one-fifth less than it did at the commencement. If a portion of this residual air be decanted into another jar, it will be found to be unfit for the support of animal life; a mouse or other small animal introduced into it speedily dies, and the flame of a candle is instantly extinguished. The gas which has been thus obtained, is an elementary body nearly in a state of purity, termed *nitrogen* (289). In this experiment the heated mercury has been slowly effecting the removal of the oxygen from the air.

§ I. Oxygen. (O=8) *Combining Volume,* 1: *Specific Gravity,* 1·1057.*

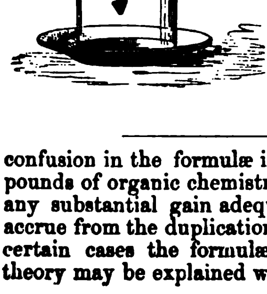
(285) If the red scales which are formed upon mercury when,

* Gerhardt proposed to double the atomic weight of oxygen, making *O*=16. Many ingenious arguments may be urged in its favour, and the proposal has been lately adopted by some chemists of distinction. Much

as in the foregoing experiment, it is heated in a confined portion of air, be introduced into a small glass retort and exposed to a strong heat, they will gradually disappear; drops of mercury will become condensed in the cool part of the retort, and a gas will be disengaged, which may be collected over water. If the experiment be performed with accuracy the quantity of the gas obtained will be exactly equal in volume to the bulk absorbed from the air by the mercury. To this gas the name of *Oxygen* ('generator of acids' from ὀξὺς 'sour,' and γεννάω 'to produce') has been given. It is an elementary body, and from the abundance in which it occurs, the number and the variety of its compounds, and the necessary part which it performs in the maintenance of life, it must be regarded as the most remarkable and important of the simple bodies.

Properties.—Oxygen possesses extremely powerful chemical affinities for other elementary substances; one element only (fluorine) being known with which it does not combine. Owing to the intensity with which many of these combinations take place, oxygen gas possesses the power of supporting combustion in an eminent degree. If a splinter of wood with a glowing spark on any part of it be plunged into the gas, the wood will instantly burst into flame, and will burn with extraordinary brilliancy. Many bodies which burn tranquilly in air often deflagrate with violence in oxygen. Phosphorus burns in it with a brilliancy which is painful to the eye, and in like manner sulphur and charcoal, if previously kindled, burn in the gas with great vehemence: many metals also burn vividly in it; a piece of potassium the size of a pea, if placed in a small copper spoon, c, fig. 243, and heated strongly by a spirit lamp, bursts into flame when plunged into the gas; if a piece of German tinder be attached to a piece of watch-spring or thin steel wire and be lighted, to start the combustion before it is introduced into the oxygen, the wire will burn with brilliant scintillations; and zinc foil burns in oxygen with an intense bluish white light.

FIG. 243.



Oxygen is essential to the support of animal life, and hence by the older chemists was termed *vital air*. A small animal will

confusion in the formulæ in use, especially in those of the complicated compounds of organic chemistry, has thus been occasioned; and it is doubtful if any substantial gain adequate to the inconveniences thus produced would accrue from the duplication of the numbers for oxygen and carbon, though in certain cases the formulæ are simplified by their use. The most refined theory may be explained with equal precision by either system of notation.

live in a confined space filled with oxygen for a longer period than in an equal bulk of air; but the gas is of too stimulating a quality to be breathed undiluted with impunity for any considerable time, and before long it produces death from over-excitement of the system.

Oxygen, like air, is destitute of colour, taste, and smell. Of all known substances it exerts the smallest refracting power upon the rays of light. Hitherto all attempts to reduce it to the liquid form by the combined application of pressure and of cold have proved fruitless. Oxygen has been proved to possess weak but decided magnetic properties, like those of iron, and like this substance its susceptibility to magnetization is diminished, or even temporarily suspended, by a sufficient elevation of temperature (275). It is heavier than the atmosphere, its specific gravity, according to Regnault, being 1·10563;* 100 cubic inches weighing 34·203 grains; it is only slightly soluble in water, which takes up about $\frac{1}{25}$th of its bulk, at 32°, and $\frac{1}{30}$th at 60°. 100 cubic inches of water, according to Bunsen, dissolving 4·11 cubic inches at 32°, and 2·99° cubic inches at 59° F.

Preparation.—There are several methods of procuring oxygen gas, the simplest of which consist in the exposure of certain metallic oxides to a high temperature, by which they are made to give up, more or less completely, the oxygen with which they had combined.

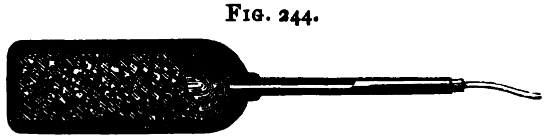
1.—The original method of Priestley, by which he first isolated pure oxygen, in 1774, consisted in heating the red oxide of mercury to 700° or 800°; but there are other modes of procuring it which are more convenient and economical.

2.—For the supply of large quantities of oxygen it is usual to employ the black oxide of manganese (MnO_2), a mineral which at a red heat parts with one-third of the oxygen which it contains, whilst a reddish brown oxide of manganese remains behind. This decomposition is expressed in symbols as follows:—

$$3\,MnO_2 \text{ give } MnO,\ Mn_2O_3 + O_2.$$

The mineral must be reduced to small fragments of about the size of a pea, and introduced into an iron bottle, fig. 244, to the neck of which an iron pipe is fitted by grinding; the bottle is heated in a furnace, and the gas is conveyed to the gas-holder by means of a piece of flexible metallic piping of

FIG. 244.



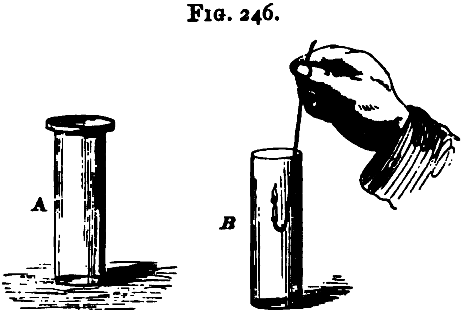
* Dumas *and Boussingault found the density of* oxygen almost exactly the *same as that given above—viz.* 1·1057; Saussure states it to be 1·1056.

suitable length. As the oxide of manganese usually contains a portion of water, and frequently also some carbonate of lime, the first effect of heat is to drive off a quantity of steam mixed with a gas which consists principally of carbonic acid. When the gas that comes off rekindles a glowing match, it may be collected for use. Black oxide of manganese, when pure, furnishes about one-ninth of its weight of oxygen; but as met with in commerce it seldom yields more than half this quantity, a pound giving off about 1400 cubic inches of the gas.

3.—A supply of very pure oxygen may also be obtained readily by the action of heat upon the salt known as chlorate of potash; 200 or 300 grains of this salt may be heated over a gas flame or a charcoal fire, in a green glass retort or in a Florence flask, F, (fig. 245), furnished with a cork which is adapted to a bent tube for delivering the gas: the salt fuses at a heat below redness, and at a temperature a little above its melting point emits a large quantity of gas, which may be collected in jars over water in the pneumatic trough, or it may, if not wanted for immediate use, be stored up in a gas-holder (38). If a jar of the gas be closed with a glass plate it may readily be inverted, as at A, fig. 246, and its power of supporting combustion tested by a taper, as shown at B. The oxygen furnished by chlorate of potash amounts to more than one-third of the weight of the salt used; 1 ounce of the crystals should yield about 512 cubic inches, or nearly 2 gallons of the gas. Chlorate of potash is a compound of chloric acid with potash; the chloric acid consists of oxygen and chlorine; the potash, of oxygen and potassium; both the chloric acid and the potash, when heated together, are

FIG. 245.

FIG. 246.



decomposed, and give up all their oxygen in the gaseous form, whilst the chlorine and potassium unite, and constitute the white salt which remains in the retort when the operation is over. The following diagram may assist in explaining these effects:—

Before decomposition.			After decomposition.
1 Eq. = 122·5 chlorate of potash (KO, ClO_5)	1 Eq. = 75·5 chloric acid ClO_5	1 Eq. = 35·5 chlorine (Cl)	1 Eq. = 74·5 chloride of potassium (KCl)
		5 Eq. = 40 oxygen (O_5)	
	1 Eq. = 47 potash, (KO)	1 Eq. = 39 potassium (K)	
		1 Eq. = 8 oxygen (O)	6 Eq. = 48 oxygen,

Or in symbols: KO, ClO_5 yield $KCl + O_6$.

4. When the quantities of chlorate employed are rather large, the heat required is apt to soften the glass of the flask in which it is decomposed. It has, however, been found that many metallic oxides, if mixed in fine powder with the pulverized chlorate in a proportion of not less than one part to ten of the salt, cause the expulsion of the gas at a much lower temperature, ranging between 450° and 500° F., although such oxides have not been proved to experience any chemical change during the operation (863). It is therefore convenient in practice to mix the chlorate of potash with about a fourth of its weight of black oxide of copper (CuO) or of manganese, that has been previously heated to redness and allowed to cool. The gas which is obtained in this way is, however, apt to contain traces of chlorine, and the heat must be carefully watched, as at a particular point the gas is disengaged with very great rapidity.

Oxygen may be obtained from various other substances, but those already mentioned are the best, and are the materials most frequently employed. Red lead and the peroxides of most of the metals, such as those of silver and lead, as well as saltpetre, when heated strongly, furnish the gas; and a mixture of sulphuric acid in its concentrated form with half its weight of powdered oxide of manganese, or of acid chromate of potash, may also be made use of by applying heat to the materials placed in a glass retort.*

* Acid chromate of potash and sulphuric acid when heated together undergo a decomposition, in consequence of which, oxygen, acid sulphate of potash, and sulphate of chromium are produced. This change may be represented in the following manner:—

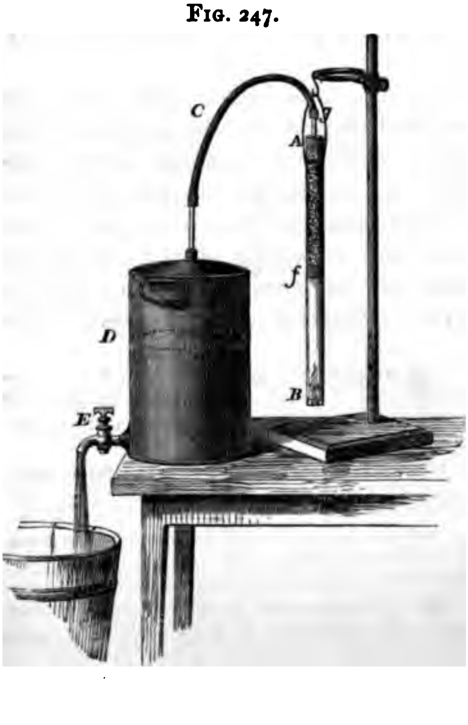
$$\overbrace{(KO, 2CrO_3)}^{\text{Acid chrom. Potash.}}+\overbrace{5(HO, SO_3)}^{\text{Sulph. Acid.}}=\overbrace{KO, HO, 2SO_3}^{\text{Acid Sulph. Potash.}}+\overbrace{Cr_2O_3, 3SO_3}^{\text{Sulph. Chrom.}}+\overbrace{4HO}^{\text{Water.}}+\overbrace{3O}^{\text{Oxgn.}}$$

Part of the sulphuric acid is employed in displacing the chromic acid from the acid chromate of potash, and in forming acid sulphate of potash in its place, whilst another portion of the sulphuric acid assists in decomposing the liberated chromic acid, which loses half its oxygen and becomes converted into oxide of chromium, and this oxide, by combining with the sulphuric acid, forms sulphate of *chromium*.

(286) *Nature of Combustion.*—The distinguishing feature of oxygen is its remarkable power of supporting combustion. Whenever any rapid chemical action attended with extrication of light and heat takes place, *combustion* is said to occur. In order to commence this action it is generally necessary to apply heat; afterwards the heat which is liberated during the process is more than sufficient to carry it on, and the act of combination proceeds with increasing rapidity. A stick of charcoal may be kept in oxygen at common temperatures for years without entering into combination with the gas, but the smallest spark upon the surface of the charcoal will suffice to determine its immediate and vivid combustion.

It must ever be borne in mind that in the case of combustion, as in every instance of chemical action, how completely soever the combustible, or body which is burned, may change its form, so as even to disappear from our sight, there is no actual destruction of matter, or loss of weight. A candle in burning seems to be completely destroyed; and when the combustion is over, an insignificant trace of ash from the wick is all that remains to the eye. It is, however, easy to show that there is no actual destruction of its components in this operation, but that the constituents of the candle in burning have combined with a certain proportion of oxygen, and that the aëriform compounds, carbonic acid and aqueous vapour, which are the result of the combustion, though invisible, really weigh more than the original candle; the gain in weight representing the quantity of oxygen which has produced the chemical change by its combination with the materials of the candle.

FIG. 247.



The experiment may be conducted in the following manner:—Take a glass tube, A B, fig. 247, 14 or 15 inches long, and $1\frac{1}{4}$ inch in diameter; thrust a piece of wire gauze, *f*, half way down the tube, and fill the

upper half with fragments of fused potash. The fused potash is employed to retain both the carbonic acid and the moisture, which are the only compounds produced by the burning candle, if it be properly supplied with air. To the lower end of the tube fit a cork perforated with three or four holes for the admission of air, and fasten to it a short piece of wax taper. To the other end of the tube adapt a cork, through which a short piece of tube, *g*, about one-third of an inch in diameter is passed. Now weigh the tube and its contents. Connect the tube *g* with a piece of flexible tubing, C, to an aspirator jar, D, filled with water; open the stopcock, E, and let the water flow. The water cannot escape at E till its place is supplied by atmospheric air; and since the aspirator, through the tube C, is connected with A B, which at B communicates freely with the atmosphere, a current of air is established through A B. Now withdraw the cork B, light the taper, and quickly replace it in the tube; in about three minutes' time close the stopcock of the aspirator: the taper is instantly extinguished. Detach the tube C; the glass A B, when cold, will weigh several grains heavier than before.

At the ordinary temperature of the atmosphere oxygen frequently enters slowly into combination without any perceptible disengagement of heat, as when a bar of iron is gradually rusting in the air. In other instances, where the process is more rapid, the heat accumulates, and sometimes it rises high enough to cause the materials to burst into flame, producing what are called cases of spontaneous combustion. Charcoal that has been reduced to fine powder as a preliminary to the manufacture of gunpowder, and which offers a large surface to the air, occasionally exhibits this phenomenon; and it is still more often manifested when tow that has been used for wiping machinery lubricated with oil is laid aside in heaps. The oil when spread over so large a surface, absorbs oxygen rapidly, and the temperature goes on rising until the mass bursts into flame.

The oxidation of the metals has been observed to take place much more rapidly in a moist than in a dry atmosphere. A bar of polished iron will remain in dry air unchanged for any length of time, but if moisture be present it will quickly become rusty; the oxide of iron in this case combines with the water which it absorbs from the air (633). In the case of iron, the oxidation continues to spread through the entire mass of the metal; but in other instances, as occurs with lead and zinc, a superficial coat of oxide is formed, which adheres firmly to the surface, and protects the metal beneath from further change.

The more the oxygen is diluted, whether by diminution of

pressure, or by mixture with a gas which does not act chemically upon it, as with the nitrogen of the atmosphere, the less elevated is the temperature which is produced in a given time by combustion, because fewer particles are in contact with the burning body, and the more slowly, in consequence, does the operation proceed. The activity of the combustion is greatly increased by increasing the number of particles of oxygen which are brought in a given time into contact with the combustible, and by carrying away the gaseous products of combustion which are incapable of combining with the fuel, and which, if suffered to accumulate, would cut off the supply of fresh oxygen; in this way the action of the smith's bellows and the blowing machine of the blast furnace may be explained. The influence of a long chimney in producing a powerful heat in the furnace at its base is similar; whilst the effect of diminishing the supply of air by closing the damper, or shutting the door of the ash-pit, is seen in the diminished temperature and reduced consumption of fuel which occurs under such circumstances.

It is, however, important to remark that the quantity of heat emitted during the combination of a given quantity of oxygen is definite, and is dependent in part upon the chemical nature of the burning body, but it is independent of the rate at which the combustion is effected. (1478 *et seq.*)

The act of respiration in animals, during which the oxygen of the air is brought into contact with the blood through the agency of the lungs, is attended with a slow change, analogous to combustion, and is accompanied by extrication of heat; an oxidation of a portion of the constituents of the blood occurs, and at the same time the colour of the blood is changed from a dusky purple to bright crimson.

All bodies may, with reference to combustion, be arranged under one of three classes. The first class consists of bodies which, like oxygen, allow other substances to burn in them freely, but which cannot themselves, in ordinary language, be set on fire: these are termed *supporters of combustion.* The second class consists of bodies which, like charcoal, actually burn when sufficiently heated in a gas belonging to the first class: these substances are termed *combustibles.* The third class embraces such bodies as will neither burn themselves nor support the combustion of others; they may be made red hot, but do not burn; sand, iron-rust, and earthy bodies in general are examples of this kind; they are for the most part compounds that have at some time or other been produced by combustion; that is, they are bodies that have been already burned, and are no longer fitted to undergo this change.

(287) *Varieties of Oxides.*—The compounds which oxygen

forms with other elements are in chemical language termed *oxides*, and a body which has combined with oxygen is said to have become *oxidized*. The number and variety of these compounds are very great, for oxygen is the most widely diffused and abundant of the elements. It constitutes about a fifth in bulk of the atmosphere; it forms eight-ninths of all the water on the globe, and it is not less extensively met with amongst the solid constituents of the earth: silica, in all its varieties of sand, flint, quartz, rock crystal, &c.—chalk, limestone, and marble—and all the various kinds of clay, each contain about half their weight of oxygen. In the forms of animal and vegetable life it is also equally generally diffused; it is indeed absolutely essential to the maintenance of the vital functions in both; and although not the only body which is fitted to support combustion, it is, from its existence in the atmosphere, the element which, in the vast majority of cases, maintains combustion on the surface of our planet.

Amongst the varied compounds formed by oxygen it is remarkable that there exist two classes which are in chemical properties directly opposed to each other. Many substances, like phosphorus, by their combination with oxygen, yield a compound which is freely soluble in water, has a sour, burning taste, and turns many vegetable blue colours, such as the blue of an infusion of litmus or of purple cabbage, to a bright red, and which, in short, possesses the characters of an *acid*. All the elements which are not metallic, with the exception of hydrogen and of fluorine, form with oxygen one or more acid compounds. Most of the metals, however, by their union with oxygen, give rise to bodies of an opposite kind, which have been termed *bases*. Potassium, for example, when burned in oxygen, furnishes a white alkaline substance, which is dissolved rapidly by water, and produces a colourless liquid, of a soapy, disagreeable taste, and a peculiar lixivial smell; it has a caustic action on the skin, restores the blue colour to litmus which has been reddened by an acid, and it completely neutralizes the strongest acids. Other metals form oxides, which, though not soluble in water, nevertheless preserve their basic character, and saturate the acids perfectly. Protoxide of iron, for instance, is soluble in sulphuric acid, and forms with it a crystalline salt. It is found that when an element combines with oxygen to form an acid, it unites with a larger number of equivalents of oxygen than when a base is the result of the combination.

Intermediate between the acids and bases is a third class of oxides, which are indisposed to enter into combination with either acids or bases. *The black oxide of* manganese (MnO_2), the mag-

netic oxide of iron (FeO, Fe_2O_3) and red lead ($2PbO, PbO_2$), may be mentioned as instances of this kind: such oxides are often produced by the union of two other oxides with each other. These indifferent oxides are sometimes termed *saline* oxides, from their analogy to salts in composition.

(288) OZONE.—When a succession of electric sparks is transmitted through atmospheric air or through dry oxygen, a peculiar odour is perceived, which has by some been compared to that of weak chlorine. To the body which produces it Schönbein gave the name of *ozone*, from the circumstance of its possessing a powerful odour. Opinions upon the cause of this odour were long divided; but the concurrent observations of several accurate experimentalists seem to indicate that it is owing to a modification produced in oxygen itself, by which it is made to assume a more active condition. One of the easiest methods of exhibiting the production of ozone consists in transmitting a current of oxygen through a tube into which a pair of platinum wires is sealed, with the points at a little distance apart: on connecting one of the wires with the prime conductor of an electrical machine in good action, whilst the other wire is in conducting communication with the earth, the peculiar odour of ozone is immediately developed in the issuing gas; but notwithstanding the powerful odour thus produced, a minute portion only of the oxygen undergoes this change. Andrews and Tait (*Phil. Trans.* 1860) have shown that in order to produce the maximum effect in electrifying oxygen, it is necessary to transmit the discharge *silently*. By operating in sealed tubes upon pure and dry oxygen, they succeeded, when great care was taken to prevent the transmission of sparks, in converting a large portion of the gas into ozone. Ozone is much denser than oxygen itself; by a continuous electrical discharge maintained for many hours, they succeeded in effecting a contraction in bulk of the gas amounting to one-twelfth of the entire volume operated on; and on heating this gas to 550 F. the ozone disappeared, whilst the oxygen resumed its original volume. The passage of the electric *spark* also immediately destroys a large proportion of the ozone which had been previously produced: Andrews and Tait, however, hesitate in admitting the hypothesis that ozone is an allotropic form of oxygen, and they have suggested the possibility that in these experiments the oxygen may be decomposed into ozone, and some other substance not at present recognised.

Great difficulties, however, lie in the way of this supposition, for ozone may be obtained without the aid of electricity. Houzeau states that the oxygen evolved from peroxide of barium by the addition of oil of vitriol, contains ozone; it has a powerful odour,

and he found that it oxidizes ammonia, and kindles the less inflammable variety of phosphuretted hydrogen (376); after it has been heated it no longer possesses these properties.*

If a stick of clean phosphorus, moistened with a few drops of water, be placed in a bottle of atmospheric air, the slow oxidation of the phosphorus is attended with the production of ozone: in an hour or two this attains its maximum. If the phosphorus be not then removed, the ozone by degrees disappears, owing to its combination with the phosphorus. No ozone is formed if the air be perfectly dry, and dry oxygen is not ozonized by phosphorus. It is also probable that ozone is formed in other slow oxidations, such as that of ether, and of oil of turpentine. Schönbein appears to have proved that in all these cases the formation of ozone is accompanied by that of binoxide of hydrogen, a fact which is true also of electrolytic ozone. Ozone, as obtained by any of these processes, is present in but very minute quantity, being diluted with from 50 to 200 times its volume of oxygen.

When diluted sulphuric acid, or a solution of the sulphates, chromates, phosphates, and several other salts of the alkalies, is decomposed electrolytically between plates of platinum or gold by the voltaic battery, the oxygen which is evolved has a powerful odour of ozone. The experiments of Andrews (*Phil. Trans.*, 1855 and 1860) appear to have established the identity of the ozone obtained by the electricity of the machine, with that produced by voltaic action, as well as with that obtained by the decomposition of peroxide of barium, and by the oxidation of phosphorus, although it was maintained by Baumert (*Poggend. Annal.*, lxxxix. 38) that electrolytic ozone contained a peculiar peroxide of hydrogen, as Schönbein himself at one time supposed.

Properties.—Ozone is insoluble in water, and in solutions either of acids or alkalies. Air charged with ozone exerts an irritating

* The reader is referred for Schönbein's speculations upon the existence of two opposite forms of oxygen, ozone and *antozone*, to the *Phil. Mag.* for 1858. They are ingenious, but although the existence of two oppositely polarized forms had previously been rendered probable by the experiments of Brodie and others, it is not very probable that ozone is the isolated form of one of these bodies. A mixture of a solution of permanganate of potash with one of peroxide of hydrogen evolves oxygen, whilst hydrated peroxide of manganese is precipitated; and in like manner a solution of chromic acid acidulated with sulphuric acid gives off oxygen on the addition of peroxide of hydrogen, whilst green sulphate of chromium is produced. Hence it has been supposed that the oxygen in the permanganic or chromic acid, is in an opposite polar condition to the second atom of oxygen in the peroxide of hydrogen; the tendency to union between these two supposed oppositely polar forms of oxygen is conceived to be the cause of the decomposition, and the result of their union is the gaseous oxygen which escapes.

action upon the respiratory organs. Ozone possesses considerable bleaching powers, acts rapidly as a powerful oxidizing agent, and corrodes organic matters, such as the cork or caoutchouc used in connecting the different parts of the apparatus together: fragments of iron, of copper, and even of silver when moistened, rapidly absorb it and become converted on their surface into oxides; silver even becomes a peroxide, though this metal does not enter into direct combination with ordinary oxygen either when moist or dry. When the ozone and the metals are perfectly dry, little or no absorption of ozone occurs. Dry iodine, also, immediately removes ozone. It is remarkable that no contraction follows the absorption of ozone by this, or by any other agent; this point was carefully and minutely observed by Andrews and Tait. Hence it seems to be probable that the ozone is resolved into a quantity of ordinary oxygen, equal in bulk to itself, which is liberated at the moment that another portion of oxygen enters into combination with the iodine. Ozone displaces iodine from its combinations with the metals, setting the iodine at liberty; indeed, this reaction is so easily produced that it furnishes the readiest and most delicate method of detecting the presence of traces of ozone in the air; a slip of paper moistened with starch and iodide of potassium, and inserted into a vessel containing the smallest admixture of ozone, becomes blue from the action of the liberated iodine, which immediately unites with the starch, and forms the blue iodide of starch which is so characteristic of iodine. Indeed, pure oxygen contained in a tube inverted over a solution of iodide of potassium, is entirely absorbed by the liquid, if the gases be subjected to the passage of electrical sparks through it for a sufficient length of time. Paper soaked in a solution of sulphate of manganese (MnO, SO_3) likewise shows the presence of ozone by becoming brown, owing to the manganese which exists as protoxide in the sulphate assuming an additional equivalent of oxygen, and becoming converted into the insoluble hydrated peroxide. If the paper be stained black with sulphide of lead ($Pb\,S$), this stain will gradually disappear; both the sulphur and the lead will absorb the ozone, or active oxygen, and a white sulphate of lead (PbO, SO_3) will be formed. One of the most singular circumstances connected with ozone is the effect of heat upon it. A temperature not much higher than that of boiling water is sufficient slowly to destroy all its active character, and the change is instantaneous at the temperature of 570°. By placing the flame of a spirit-lamp so as to heat a part of the tube through which the electrified oxygen escapes, all signs of ozone disappear. Ozonized air is also deozonized by transmission over cold peroxide of manganese.

If a piece of paper, soaked in a mixture of starch and iodide of potassium be exposed in the open air for five or ten minutes, it often acquires a blue tint, the intensity of which varies on different days; sometimes, particularly in damp or foggy weather, no change is produced by such exposure. These effects are plausibly supposed to be owing to the presence of traces of ozone in the atmosphere; and theorists are not wanting who believe they have traced the prevalence of cholera and other epidemics to the unusual absence of ozone in the air, during lengthened periods. Iodine may, however, be liberated from iodide of potassium by nitrous acid, by chlorine, and by various agents besides ozone, so that this reaction, although a very sensitive one for ozone, is by no means characteristic of its presence; and the existence of traces of ozone in the atmosphere, probable though it is, cannot be said to have been unequivocally proved.

§ II. Nitrogen.

N = 14; *Comb. Vol.*, 2; *Sp. Gr.*, 0·9713.

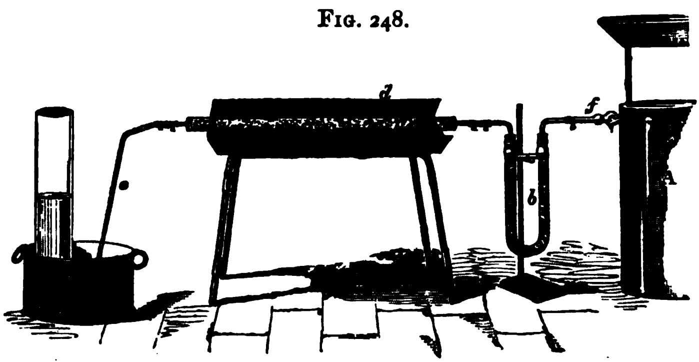
(289) It has already been observed (284) that the larger proportion of the atmosphere consists of a gaseous body, which has been named *nitrogen* ('generator of nitre'), because it is an essential constituent of nitre: sometimes the name of *azote* (from *α*, 'not,' ζωή, 'life,') is given to it, because, though not poisonous, it is incapable of supporting life. This element was discovered by Rutherford in 1772.

Properties.—Nitrogen is a colourless, tasteless, and inodorous gas, which as yet has resisted every effort to liquefy it. It is somewhat lighter than atmospheric air; calculating from Regnault's experiments, 100 cubic inches at 60° F. Bar. 30° in., weigh 30·119 grains. Water dissolves not more than $\frac{1}{50}$ of its bulk of this gas at ordinary temperatures, 100 cubic inches of water at 32° absorbing 2·03 cubic inches of nitrogen, and 1·48 cubic inches at 59° (Bunsen). No two substances can offer a more striking contrast in chemical properties than oxygen and nitrogen: the one the most energetic of the elements, the other the most indifferent. It extinguishes a taper without taking fire itself; an animal immersed in the undiluted gas perishes quickly for want of oxygen, but it is not directly poisonous; indeed, it enters as a necessary component into the animal frame, and with every act of inspiration it finds admission into the lungs. One very important purpose that it fulfils in the atmosphere is the dilution of the oxygen, which is rendered thereby less stimulating to the living system, and the rapidity of ordinary combustion is likewise thereby mode-

rated. Nitrogen is one of the most extensively diffused forms of matter, as must be evident from the facts just stated; and notwithstanding its apparent indisposition to enter into combination, it forms a number of highly interesting and important compounds. For example, in combination with oxygen, it forms nitric acid, which exists as a natural production when united with potash and soda in the nitrates of those bases; it is the characteristic ingredient in ammonia; and though it occurs in but small quantity in plants, it is never entirely absent from them. Nitrogen also constitutes an essential part of many of the most potent and valuable medicines, such as quinia and morphia, as well as of some of the most dangerous poisons, as prussic acid and strychnia.

Preparation.—The most convenient methods of preparing nitrogen are based upon the removal of oxygen from atmospheric air. 1.—The simplest plan consists in placing a few fragments of phosphorus, dried by means of blotting paper, on a porcelain dish which is floated upon the surface of the water of the pneumatic trough; the phosphorus is ignited by touching it with a hot wire, and a glass receiver filled with air is then inverted over it. The phosphorus burns at the expense of the oxygen in the confined air, and being partially converted into vapour by the heat which attends the combustion, is diffused through the gas, and thus quickly searches out and combines with every portion of oxygen: when cold, the nitrogen may be decanted into another jar and examined. 2.—The removal of oxygen from the air may also be effected more slowly in various ways; a stick of phosphorus will, if introduced into a jar of air which is standing over water, slowly absorb the oxygen, and in two or three days about four-fifths of the original bulk of the air, consisting of nitrogen nearly pure, will be left. 3.—Moistened iron filings produce a similar result, the metal gradually becoming oxidized, as is seen by the rusty

FIG. 248.



appearance which it assumes. 4.—When larger quantities of nitrogen are required, metallic copper may be employed to absorb the oxygen. The method to be adopted in this case is exhibited in fig. 248. *c* represents a long straight tube of hard glass, which will resist a strong heat without fusion; it is filled with metallic copper in a finely divided state; for this purpose the metal which has been reduced from the powdered oxide by means of hydrogen gas is well adapted. The tube *c* rests on a sheet-iron furnace, *d*, in which it can be surrounded by charcoal and raised to a red heat; *e* is a bent tube for delivering the gas into a jar over water or mercury; the other extremity of the tube *c* is connected with a bent tube, *b*, filled with fragments of fused caustic potash; and the air which supplies the nitrogen is driven from the gas-holder, A, over the ignited copper in a stream which is easily regulated by the stop-cock, *f*. The air is first driven over the fused potash, where it leaves all traces of carbonic acid and of moisture, it then passes over the ignited copper, by which every portion of oxygen is completely removed. 5 and 6.—Nitrogen may also be obtained by the action of chlorine on a solution of ammonia (325), and it is furnished in a state of equal purity by heating the nitrite of ammonia (311).

§ III. Composition of the Atmosphere.

(290) If a mixture be made of 4 measures of nitrogen and 1 measure of oxygen gas, a candle will burn in it as in atmospheric air; it may be breathed as air, and possesses the ordinary properties of the air. The atmosphere is in short a mechanical mixture of several gases, amongst which oxygen and nitrogen constitute the principal portions, and which, notwithstanding their difference in density, are, owing to the principle of diffusion (64), uniformly mixed with each other. Chemical operations are continually occurring upon the earth's surface, which remove oxygen and add a variety of other gases, amongst which carbonic acid is the most abundant. Yet so beautifully adjusted is the balance of chemical actions over the face of the earth, that no perceptible change in the composition of the atmosphere has been observed since accurate experiment on the subject has been practised.

Air which has been freed from carbonic acid and aqueous vapour consists, according to the numerous careful analyses of Dumas and Boussingault (*Ann. de Chimie,* III., iii., 257), on an average of 20·81 of oxygen by measure, and 79·19 of nitrogen in 100·00 parts, or by weight of 23·01 of oxygen, and 76·99 of nitrogen. These experiments were performed by allowing the air to stream slowly *over a weighed quantity* of heated copper, whereby

the oxygen was absorbed (fig. 248) whilst the nitrogen was received into an exhausted flask, which was weighed before the experiment was commenced and after its termination; the quantity of oxygen was found by the gain in weight experienced by the tube containing the copper. The results obtained by Regnault, Brunner, Verver, and others, by different methods of analysis, do not vary more than $\frac{1}{500}$ from the quantity of oxygen just mentioned. Trifling temporary variations no doubt occur from local causes; but the air brought by Gay-Lussac from an elevation of four miles above the surface of the earth, that collected on the summit of the Alps, and that examined both in town and country in various parts of the globe, presents no sensible difference from the mean above given.*

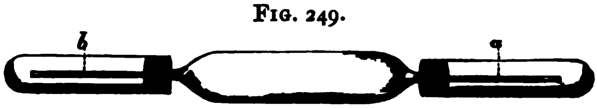
100 cubic inches of dry air weigh at 60° F. and 30 inches Bar., calculating from the experiments

of Dumas and Boussingault	31·086	grs.
of Biot and Arago	31·074	„
of Prout	31·0117	„
of Regnault	30·935	„

The second result is probably the most accurate, for it exactly corresponds with the density deduced from that of a mixture of oxygen and nitrogen in the proportions in which they occur in the atmosphere. The weight of a given volume of air at 60° F., under a pressure of 30 inches Bar., is therefore only $\frac{1}{816}$ of that of an equal bulk of water at the same temperature. Owing to the

* A portion of air collected by Mr. Welsh, in August, 1852, at an elevation of 18,000 feet, in one of the balloon ascents undertaken by him and Mr. Green under the direction of the Kew Committee of the British Association, contained 20·88 per cent. of oxygen by volume, while air collected at the surface at the same time contained 20·92. The air was collected in tubes of about 6 cubic inches in capacity, fitted with accurate stopcocks. They were exhausted previously to the ascent, and were filled with the air for examination by opening the stopcocks, which were again closed as soon as the charge had entered. In the extensive series of experiments of Regnault (*Ann. de Chimie*, III., xxxvi., 385), air was collected at different points of the earth's surface in glass tubes, drawn out to an open capillary extremity at either end, fig. 249. When a specimen of air was to be collected, one of these tubes was

FIG. 249.



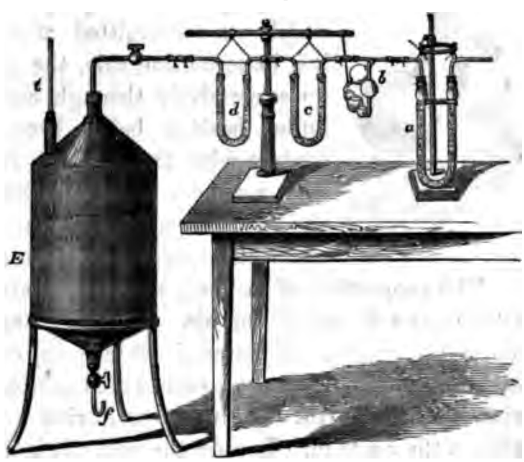
attached by a flexible tube to a small pair of bellows, and by working the bellows a few times, the tube was filled with air of the locality. The capillary tubes were then drawn off and sealed, as at *a* and *b*, by momentary contact with the flame of a spirit-lamp, and the closed ends were protected from injury during the journey by small caps of glass tube fitted with corks. The analyses of the air thus obtained were executed by means of hydrogen, in a eudiometer of Regnault's contrivance. The same apparatus was used by myself in the analyses of the air collected by Mr. Welsh.

greater solubility of oxygen than of nitrogen, rain water and melted snow always contain a larger proportion of oxygen than the air itself, amounting to about 34 per cent. of the air dissolved, or nearly two volumes of nitrogen to one volume of oxygen. This is a circumstance of great importance to aquatic animals, and one which could occur only in consequence of the air being a mechanical mixture and not a chemical compound of the two gases.

In addition to oxygen and nitrogen the atmosphere contains a certain proportion of carbonic acid, a variable but minute trace of ammonia, traces of nitric acid, and of some compound of carbon and hydrogen, and frequently in towns a perceptible amount either of sulphurous acid or of sulphuretted hydrogen. Aqueous vapour is of course also present at all times, although its amount is liable to extensive fluctuations.

(290 *a*) The amount of aqueous vapour at any spot may be ascertained by means of the hygrometer (181), or it may be determined by a direct experiment in the following manner. A bent tube, *a*, fig. 250, filled with pumice stone moistened with sulphuric acid, is connected with a vessel, E, of known capacity; suppose it be capable of containing 18 gallons of water. This vessel having been filled with water, is allowed to empty itself slowly by opening a stopcock, *f*, which terminates in a tube bent upwards to prevent the entrance of air at the bottom; a known volume of air is thus drawn through the tube *a*, which retains all the moisture. If the weight of this tube be determined before commencing the experiment, and a second time after it is completed, the increase in weight will indicate the amount of moisture in the bulk of air operated upon. The temperature is ascertained by means of the thermometer, *t*, and the atmospheric pressure is obtained by an observation of the barometer at the time. The flow of water by the aspirator is rendered uniform during the whole course of the experiment

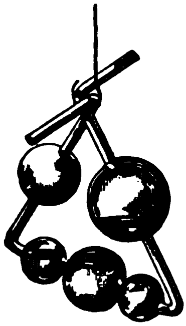
FIG. 250.



by making the tube which conveys the air sufficiently long to reach nearly to the bottom of the vessel, as shown by the dotted line which passes down from the central opening at the top.

(290 *b*) The quantity of carbonic acid in the air may be determined in the course of the same experiment. If the bulbs at *b* be filled with a strong solution of caustic potash (sp. gr. 1·25), and the tube *c*, with fragments of fused potash, the gain in weight experienced by the tubes, *b* and *c*, will indicate the quantity of carbonic acid which has been absorbed in the operation: the bent tube, *d*, is filled with pumice-stone moistened with sulphuric acid; it is not weighed, but is merely interposed as a measure of precaution between the aspirator E, and the tube *c*, to prevent any accidental trace of moisture from passing backwards into *c*. The bulbs seen at *b* are to be filled with potash to the extent shown in the enlarged drawing, fig. 251. This form of apparatus was contrived by Liebig. It is in continual requisition in the laboratory, for the purpose of absorbing gases which are transmitted through it; by placing it a little on one side, the gas is made to bubble up successively through each of the three lower bulbs, besides being brought thoroughly into contact with the liquid in the narrow portions of tubing which connect the different bulbs together. This simple contrivance has added greatly to precision in experiments of this kind.*

FIG. 251.



The proportion of carbonic acid in the atmosphere varies from 3 to 6 parts in 10,000 of air. Saussure found that within these limits its amount is lessened after rain, owing to the solvent action of the descending shower, which carries a portion of the gas with it to the earth. It increases during a frost, and diminishes when a thaw sets in. During the night it increases, and diminishes again after sunrise. It is less in amount over large bodies of water than over large tracts of land. The proportion of carbonic acid is less liable to vary on elevated mountains, where it is generally more abundant than in the plains. It is also more abundant

* Pettenkofer estimates the quantity of carbonic acid in air by agitating a given volume of the air for trial with a measured amount of lime-water of known strength. The lime-water used for this purpose is graduated by the alkalimetric method, by means of a standard solution of oxalic acid. The carbonic acid neutralizes and precipitates a certain quantity of lime in the form of chalk, and the quantity of lime which remains in the solution after the experiment, is again determined by the solution of oxalic acid. The difference in the quantity of lime before and after its action upon the air, enables the operator to calculate the proportion of carbonic acid with great accuracy.

in densely populated districts than in the open country. In inhabited dwellings, and in rooms for public assemblies, the proportion of carbonic acid may, however, greatly exceed the normal amount.

The quantity of ammonia and nitric acid in the atmosphere is materially diminished after long-continued and heavy rains. Occasionally, from local and accidental circumstances, other gases and vapours are also met with. The air of towns contains in addition certain organic impurities in suspension. Dr. Angus Smith has attempted to estimate their amount by measuring the quantity of a very dilute solution of permanganate of potash of known strength which a given bulk of air will deprive of colour.—(*Q. J. Chem. Soc.*, xi. 217.) The average composition of the atmosphere in the climate of England may, however, be stated as follows, in 100 parts by volume:—

Average Composition of the Atmosphere.

	Oxygen	20·61
	Nitrogen	77·95
	Carbonic acid	·04
	Aqueous vapour	1·40
	Nitric acid	traces
	Ammonia	
	Carburetted hydrogen	
and in towns	Sulphuretted hydrogen	traces
	Sulphurous acid	

CHAPTER III.

WATER. HYDROGEN.

§ I. Water. (HO = 9)

*Comb. Vol. as Vapour, 2; Sp. Gr. as Vapour 0·622, as Liquid 1·000, as Ice 0·94.**

(291) On the uses of water it is almost needless to enlarge, for they are universally felt and appreciated. In each of its three physical conditions, the blessings which it confers upon man are inestimable. As ice, it furnishes in northern lands for months together, a solid bridge of communication between distant places: in the liquid condition, it is absolutely necessary to the existence of vegetable and animal life; in this shape, too, it furnishes to man a continual source of power in the flow of streams and rivers; it supplies one of the most convenient channels of communication between places widely separated; and further, it is the storehouse

* Gerhardt represents the composition of water as H_2O ($O=16$); making its atomic weight 18, in which case the combining volume of its vapour $=4$, if the volume of $O=8$ be taken $=1$.

of countless myriads of creatures fitted for use as food: in the state of vapour, as applied in the steam-engine, it has furnished a power which has in later years done more than any other physical agent to advance civilization, to economize time, and to ameliorate the social condition of man. In each and all of these points, if rightly considered, we must perceive the entire adaptation of this wonderful compound to the ends which it was designed by the Creator to fulfil.

Glancing at the physical condition of our planet, we cannot fail to be impressed with the important effects produced by the movements of water at periods anterior to the existence of man, as well as in more recent times. To such causes must we refer the formation of sedimentary rocks and their arrangement in successive strata upon the surface of the earth: even now, observation shows that denudation is proceeding at some points, elevation and filling up of hollows at others; whilst the accumulation of drift and a variety of other extensive geological changes must be traced to the same ever acting and widely operating agency.

It may further be observed that there is no form of matter which contributes so largely as water to the beauty and variety of the globe which we inhabit. In its solid state we are familiar with it in the form of blocks of ice, of sleet and hail, of hoar frost fringing every shrub and blade of grass, or of snow protecting the tender plant, as with a fleecy mantle, from the piercing frosts of winter. The rare but splendid spectacles of mock suns, or parhelia, are due to the refractive power of floating spiculæ of ice upon the sun's rays. In its liquid condition, as rain or dew, it bathes the soil: and the personal experience of all will testify to the charm which the waterfall, the rivulet, the stream, or the lake adds to the beauty of the landscape; whilst few can behold unmoved the unbounded expanse of ocean; which whether motionless, or heaving with the gently undulating tide, or when lashed into foam by the storm that sweeps over its surface, seems to remind man of his own insignificance, and of the power of Him who alone can lift up or quell its roaring waves. In vapour how much variety is added to the view by the mist or the cloud; which by their ever-changing shadows diversify, at every movement, the landscape over which they are flitting; whilst the gorgeous hues of the clouds around the setting sun, and the glowing tints of the rainbow, are due to the refractive action of water and watery vapour upon the solar rays.

Properties.—At the ordinary temperature of the air, water, when free from admixture, is a clear, colourless, transparent liquid, destitute of taste or smell. At temperatures below 32° it freezes

and assumes a variety of crystalline forms derived from the rhombohedron and six-sided prism. Water evaporates at all temperatures, and under the ordinary pressure of the atmosphere it boils at about 212°. Its anomalous expansion by heat (137), and the important purposes thereby attained (145), as well as the great dilatation which it undergoes on freezing (73), have been already pointed out. Arago and Fresnel have shown, that notwithstanding the gradual dilatation of water at temperatures below 39°, its refractive power on light continues to increase regularly, as though it contracted. Its density at 60° is taken as 1·000, and it forms the standard with which, in this country, the specific gravities of all solids and liquids are compared. A cubic inch of water at 60° F. weighs in air 252·456 grains.

To the chemist water is invaluable as a solvent. It is the perfection of a neutral substance; and it enters into combination most extensively both with acids and with bases. Experience has shown that when an acid has once been allowed to combine with water, the entire separation of the water from the acid is seldom practicable, unless some powerful base be presented to the acid; in such a case the base displaces the water, and its expulsion by heat is then easily effected. Suppose, for example, that sulphuric acid has been freely diluted with water; upon the application of heat the water at first passes off readily, leaving the less volatile acid behind. By degrees, however, it becomes necessary to increase the temperature in order to expel the water, and at last the acid begins to evaporate also, and finally no further separation can be effected, because when the temperature rises to about 640° F. both water and acid distil over together. It is found on analysing the acid when it has reached this point, that the liquid contains one equivalent of acid and one of water (HO, SO_3). But if to this concentrated acid an equivalent of potash, or one of oxide of lead, be added, the water is easily expelled, and an equivalent of anhydrous sulphate of potash (KO, SO_3) or of sulphate of lead (PbO, SO_3), is obtained. Water which, as in the foregoing instance, supplies the place of a base in combination with acids, is called *basic* water.

In a similar manner water combines with the powerful bases, such as potash or soda, and then cannot be expelled from them until some acid has been added. Potash in the form in which it is obtained by evaporating down its aqueous solution and heating the residue to dull redness, consists of one equivalent of the alkali and one of water (KO, HO), and this equivalent of water cannot be expelled except by the addition of an acid, such as sulphuric acid; then by *the application of* heat, anhydrous sulphate

of potash is obtained. In this case the water in combination with the base performs the part of an *acid*.

The compounds of water are frequently termed *hydrates*. When a body is described as being entirely free from water in combination, it is commonly said to be *anhydrous*.

Many salts in crystallizing unite with a definite quantity of water, which is essential to the form of the salt, but which may, by the application of a gentle heat, be expelled without altering the chemical properties of the saline body. In this case the water is spoken of as *water of crystallization*. Many salts part with such water by mere exposure to air. Carbonate of soda, for example, crumbles down or *effloresces* to a white powder; and the same thing occurs in the case of sulphate of soda.* The form of the salt depends upon the quantity of this water of crystallization. For instance, borax is always found to crystallize with 10 equivalents of water ($NaO, 2\,BO_3 + 10\,Aq$), in oblique rectangular prisms, if the solution of the salt be not sufficiently concentrated to begin to crystallize till the temperature falls to 133° F.; but from a more concentrated solution borax is deposited in regular octohedra with only 5 equivalents of water. So, again, the sulphate of soda crystallizes, under ordinary circumstances, in oblique four-sided prisms with 10 equivalents of water ($NaO, SO_3 + 10\,Aq$), but if a solution, saturated at 91°, be very slowly raised to 212°, the sulphate of soda is deposited in rhombic octohedra which contain no water.

(292) *Various kinds of Natural Waters.*—Owing to its extensive solvent powers, water is never met with naturally in a state of purity. *Rain water*, collected after a long continuance of wet weather, approaches nearest to it, but even that always contains atmospheric air, and the gases floating in the air, to the extent of about 2½ cubic inches of air in 100 of water.†

Spring Water, although it may be perfectly transparent, always contains more or less of saline matter dissolved in it; the nature of these salts will of course vary with the character of the soil through which the water percolates. The most usual saline impurities are carbonate of lime, common salt, sulphate of lime, and sulphate and carbonate of magnesia. The waters of the New Red Sandstone are impregnated to a greater or less extent with sulphate of lime. Most spring waters are charged with a notable

* Other salts, on the contrary, absorb moisture from the atmosphere, and become damp or even liquefy in the water so absorbed; they are then said to *deliquesce*. Carbonate of potash and chloride of calcium offer instances of this kind.

† The quantity of air which is contained in spring or other water can be

proportion of carbonic acid, which dissolves a considerable amount of carbonate of lime: the calcareous springs in the chalk districts around London contain from 18 to 20 grains of chalk per gallon, 6 or 8 grains of which become separated by exposure of the water

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readily ascertained in the following manner. A globular flask, *a*, fig. 252, capable of containing 14 or 16 ounces, such as is used for taking the density of vapours, is filled with the water to be examined, and connected by a vulcanized caoutchouc tube, *b*, to a piece of barometer tube, upon which is blown a bulb, *c*, 2 inches or more in diameter. This tube is bent in the manner represented in the figure; the longer limb being upwards of 30 inches in length, and terminating below in a recurved extremity designed to deliver the gas disengaged from the water, into a graduated jar, *d*, with an expanded funnel-shaped mouth, which is supported in a small mercurial bath. The bulb, *c*, having been about half filled with the water, is connected with the flask by the caoutchouc tube, which is firmly secured at both ends by ligatures. A small wooden vice, such as is seen at *f*, is made use of to compress the vulcanized tube and to cut off communication between the flask and the bulb, *c*. The water in *c* is now made to boil briskly for ten minutes or a quarter of an hour, until all the air is expelled from the tube, the mouth of which is kept just below the surface of the mercury. When, after a few minutes, continued boiling, no more air escapes from the tube, the jar, *d*, is filled with mercury and placed over the end of the long tube. The vice is removed, and heat applied to the flask; the water speedily begins to give off gas; and the quantity increases till the water boils. The ebullition must be continued steadily for a full hour, and the operation terminated by a few minutes' brisk boiling, by which the delivery tube will be filled with steam, and all the air will be driven over into the jar. One object of the globe, *c*, is to prevent the water from boiling over into the jar, *d*: a little steam always condenses in the jar above the mercury, but this is a matter of small consequence. When the operation has terminated, the gas is allowed to cool, and is transferred to a tall jar of water, or of mercury, where its bulk can be measured.

FIG. 252.

It will be found that all water, including even that which has been recently distilled, contains air. For example, three samples of water twice distilled in glass vessels, were submitted to experiment: 100 cub. in. of the first specimen contained 1·85 cub. in. of air; in the same bulk of the second 2·15, and the third specimen 2·38 cub. in. of air were present; the oxygen and nitrogen being in each case almost exactly in the proportion of 1 measure of oxygen to 2 measures of nitrogen.

to the atmosphere, so that a running stream will seldom contain more than 12 or 14 grains of chalk per gallon in solution. Waters which have filtered through a bed of chalk also often contain carbonate of soda in considerable quantity, as is the case with the deep-well waters of London.

Mineral Waters are waters impregnated with a large proportion of any one of the above-named salts, or with some substance not so commonly met with; such waters are usually reputed to possess some medicinal quality, varying with the nature of the salt in solution. Many of these springs are of a temperature considerably higher than that of the surface of the earth where they make their appearance. At Carlsbad and Aix-la-Chapelle this temperature varies from 160° to 190°. Such hot springs either occur in the vicinity of volcanoes, and then generally abound in carbonic acid, and common salt, and other salts of soda: or they spring from great depths in the rocks of the earliest geological periods, and contain chlorides of calcium and magnesium, and almost always traces of sulphuretted hydrogen. (Berzelius.)

Many mineral waters contain oxide of iron, which imparts to them an inky taste; they are then frequently termed *chalybeate* waters; some of the Cheltenham springs are of this kind. In other instances carbonic acid is very abundant, giving the brisk *effervescent* character noticed in Seltzer water. Less frequently, as in the Harrogate water, sulphuretted hydrogen is the predominating ingredient, giving the nauseous taste and smell to such *sulphureous* waters. In other instances the springs are merely *saline*, and contain purgative salts, like the springs at Epsom, which abound in sulphate of magnesia, and at Cheltenham, where common salt and sulphate of soda are the predominant constituents. Many of these saline springs also contain small quantities of iodine and bromine, which add greatly to their therapeutic activity.

River Water is less fitted for drinking than ordinary spring water, although it often contains a smaller amount of salts; for it usually holds in solution a much larger proportion of organic matter of vegetable origin, derived from the extensive surface of country which has been drained by the stream. If the sewerage of large towns situated on the banks be allowed to pass into the stream, it is of course still less fit for domestic use. Running water is, however, endowed with a self-purifying power of the highest importance; the continual exposure of fresh surfaces to the action of the atmosphere promotes the oxidation of the organic matter, and if the stream be unpolluted by the influx of the sewerage of a large town, this process is generally fully adequate

to preserve it in a wholesome state. River water almost always requires filtration through sand before it is fit for domestic use; and if water-works designed to supply such water be properly constructed, provision is made for this filtration. Suspended matters, such as weeds, fish-spawn, leaves, and finely-divided silt or mud, are thus removed; but vegetable colouring matter in solution, salts, and other bodies, when once they are dissolved, cannot be arrested by the filter.

The magnetic oxide of iron, however, appears to exert a peculiar influence in promoting the oxidation of organic matter contained in water which is allowed to percolate through it, and it appears to be probable that this action, to which Mr. Spencer has particularly called attention, may furnish a valuable auxiliary to the methods of filtration at present in use. Filtration through beds of iron turnings has likewise been practised in some cases with advantages of a similar description, but the oxygen is in this case in great measure absorbed from the water by the iron.

The presence of organic matter in water is easily ascertained by the reducing influence which it exerts upon chloride of silver or of gold, or upon permanganate of potash, when boiled with them. The chloride of silver becomes purplish; and chloride of gold imparts a brown tint to the water under such circumstances, owing to the precipitation of metallic gold. A very dilute solution of permanganate of potash (666) is rendered colourless, whilst a brown precipitate of hydrated peroxide of manganese is formed.

Water is familiarly spoken of as *hard* or *soft*, according to its action on soap. Those waters which contain compounds of lime or magnesia occasion a *curdling* of the soap, as these earths produce with the fatty acid contained in the soap a substance not soluble in water (1142). Soft waters do not contain these earths, and dissolve the soap without difficulty. Many hard waters become softer by boiling; in such cases the carbonic acid is expelled, and the carbonate and part of the sulphate of lime which were held in solution are deposited, and cause a fur or incrustation upon the inside of the boiler (542).

Sea Water is largely impregnated with common salt, and with chloride of magnesium, to which it owes its saline bitter taste. It might be supposed that the quantity of salts which it contains is continually on the increase, as the sea is the receptacle for all the fixed contents of the river water which is discharged into the ocean, since pure water alone evaporates from its surface; but here also there is a return to the surface of the soil provided for in the marine plants, the fish, and their representative guano, which are perpetually being raised from its depths by the force of storms, by

predatory birds, and by the industry of man. The specific gravity of sea water is subject to trifling variations, according to the part of the globe from which it is taken. The waters of the Baltic and of the Black Sea are less salt than the average, while those of the Mediterranean are more so. The waters of the Mediterranean in the Levant are more salt than those of the same sea near the Straits of Gibraltar. The mean specific gravity of sea water is 1·027, and the quantity of salts ranges from 3·5 to 4 per cent. According to Schweitzer (*Phil. Mag.*, 1839, vol. xv. p. 58), the water of the British Channel is composed as follows:—that of the Mediterranean, analysed by Usiglio (*Ann. de Chimie*, III. xxvii. 104) will be seen to agree very closely with it in composition:—

	British Channel.		Mediterranean.
Water	963·74372	...	962·345
Chloride of sodium	28·05948	...	29·424
Chloride of potassium	0·76552	...	0·505
Chloride of magnesium	3·66658	...	3·219
Bromide of magnesium	0·02929	...	0·556
Sulphate of magnesia	2·29578	...	2·477
Sulphate of lime	1·40662	...	1·357
Carbonate of lime	0·03301	...	0·114
Iodine	traces		
Ammonia	traces		
Oxide of iron		...	0·003
	1000·00000		1000·000
Specific gravity	1027·4 at 60° F.		1025·8 at 70° F.

Minute quantities of iron have been found in the waters of the ocean, but nitric and phosphoric acids have as yet eluded the most careful observation.

For chemical purposes water is always purified by distillation, which may be effected on a small scale in glass retorts, but it is generally carried on in a copper still provided with a pewter or copper worm. Iron pipes may also be safely used for the purpose of condensation; but lead must be avoided. The still should not be employed for any other purpose. The addition of lime to the water before submitting it to distillation is useful, as it retains the excess of carbonic acid, and also traces of hydrochloric acid, which if chloride of magnesium be present are apt to come over, owing to the decomposition of this salt: the first portions of water should be rejected, because they usually contain traces of ammonia; when a few drops of distilled water are evaporated upon a slip of glass, no stain or mark should be left, otherwise some saline impurity is present.

Water was long supposed to be an elementary substance. This, however, is not the case: it is a compound of oxygen with hydrogen, in the proportion of 1 equivalent of each; its symbol is

therefore HO, and its combining number 9. When converted into vapour, 9 grains of steam occupy twice the bulk of 8 grains (or 1 equivalent) of oxygen at the same temperature; the combining volume of aqueous vapour is therefore = 2 if the combining volume of oxygen be taken as 1. Its composition is shown in the following table:—

	Symb.		By weight.		Dumas.	By vol.			Sp. gr. vap.
Hydrogen	H	=	1 or	11·11	11·12	2 or	1·0	=	0·0692
Oxygen	O	=	8	88·89	88·88	1	0·5	=	0·5528
Water	HO	=	9	100·00	100·00	2	1·0	=	0·6220

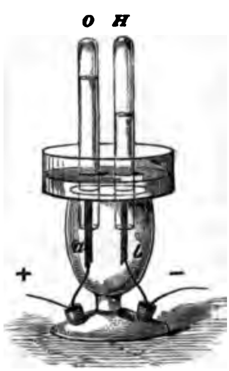
§ II. Hydrogen. (H = 1.)

Sp. Gr., 0·0692; *Comb. Vol.*, 2.

(293) *Preparation.*—The composition of water may be determined both by analysis or separation of its constituents, and by synthesis or their reunion after such separation.

1.—An elegant mode of showing the composition of water analytically is afforded by the voltaic battery. A glass vessel, fig. 253, containing two platinum plates, *a* and *b*, is filled with water, slightly acidulated with sulphuric acid to improve its conducting power, and is arranged so as to transmit the current of a battery consisting of three or four pairs of Grove's cells (233). Immediately that the two platinum plates are connected with the wires of the battery, gas rises from each; and if two similar jars be filled with water and inverted one over each plate, the volume of the gas which rises from the platinode, or negative plate, *b*, will be found to be exactly double of that which rises from the zincode, or positive plate, *a*: the gas in O will show itself to be oxygen by rekindling a glowing match, whilst that in H extinguishes flame, but takes fire itself when a light approaches it. To the latter gas the name of *hydrogen* (from ὕδωρ, water, γεννάω, to generate) has been given. Oxygen and hydrogen are the sole constituents of water, and by their union in the proportion of two measures of hydrogen to one measure of oxygen this liquid is reproduced.

Fig. 253.



2.—The presence of hydrogen and oxygen in water may be shown in other ways, and hydrogen may be obtained from it by chemical means. If a piece of sodium of the size of a pea be wrapped up in blotting paper, and be rapidly introduced beneath

the mouth of a strong wide tube, 10 or 12 inches long, filled with water and inverted in the pneumatic trough, bubbles of gas will be quickly disengaged, and will collect in the upper part of the tube. On inverting the tube and applying a light, the gas will take fire and burn with flame; the liquid in the tube will be found to be alkaline, and will change the yellow colour of turmeric to brown: soda having been formed by the combination of the sodium with oxygen derived from the water.

3.—Hydrogen may be also obtained by the action of water upon iron at a high temperature. In order to effect this, let a piece of iron piping, shown at A A, fig. 254, be filled with iron turnings, and heated to redness in a portable furnace, B; and let a current of steam be driven through the tube from a small boiler, C, attached to one extremity of the pipe; the aqueous vapour in its passage will be decomposed, the oxygen will enter into combination with the heated iron, whilst the liberated hydrogen will pass on, and may be collected over water in a jar, D, placed over the mouth of a bent tube attached to the other extremity of the iron pipe.

FIG. 254.

4.—It may also be obtained by heating zinc with a solution of potash, the metal combining with the oxygen of the water, whilst the hydrogen is liberated, the oxide of zinc as it is formed being dissolved by the alkaline liquid; but this method is interesting chiefly from its theoretical bearings rather than from any practical utility.

5.—But the most convenient way of procuring hydrogen is by the action of diluted sulphuric acid on zinc. The zinc may be melted in an iron ladle, and poured from the height of a few feet into a pail of cold water, by which means it is *granulated*, or re-

duced into grains or flakes: about half an ounce of the granulated zinc is introduced into a retort, and a diluted acid, prepared by mixing an ounce of oil of vitriol cautiously with 6 ounces of cold water, stirring all the while, is poured upon the zinc. Hydrogen gas is soon evolved in great abundance: the first portions of gas which are contaminated with the air contained in the retort, must be allowed to escape; afterwards the gas may be collected in the usual way. In this process the zinc may be regarded as taking oxygen from the water, and forming oxide of zinc, which, though insoluble in water, is immediately dissolved by the sulphuric acid, with which it forms a salt called sulphate of zinc, while the hydrogen passes off in the gaseous form. The change may be illustrated by the following diagram:—

Decomposition of Water by Zinc and Sulphuric Acid.

Before decomposition.		After decomposition.
9 = 1 eq. of water (HO)	1 = 1 eq. Hydrogen (H)	liberated.
	8 = 1 eq. Oxygen (O)	80·7 = 1 eq. sulphate of oxide of zinc (ZnO, SO_3).
32·7 = 1 eq. Zinc (Zn)		
40 = 1 eq. Sulphuric acid (SO_3)		

Or in symbols; $Zn + HO, SO_3$ give $H + ZnO, SO_3$.

An ounce of zinc is sufficient to liberate from water about 2½ gallons of the gas. Scraps of iron may be substituted for zinc; but in this case the gas is less pure: it has a disagreeable odour, due to the presence of a peculiar compound of hydrogen and carbon, but this may be removed by allowing the gas to stream through a tube filled with fragments of wood charcoal (Stenhouse). The gas furnished by the action of diluted sulphuric acid on zinc also possesses a peculiar odour, and is frequently contaminated with small quantities of compounds of hydrogen with sulphur, arsenic, and carbon. It may be freed from these impurities by causing it to pass first through a strong solution of potash, and then through a solution of corrosive sublimate, or of nitrate of silver.

Properties.—Hydrogen is an elementary substance, which was discovered by Cavendish in 1766. When obtained with the precautions just mentioned, it is a colourless, transparent, tasteless, and inodorous gas. Its refractive power upon light is higher than that of any other gas, being more than six times as great as that of atmospheric air at the same temperature, when the hydrogen is compressed till its weight is the same as that of an equal bulk of air. It has never been liquefied, and is even less soluble in water than nitrogen, 100 cubic inches of water, according to Bunsen, dissolving 1·93 cubic inches of hydrogen at all temperatures between 32° and

68° F. Hydrogen is the lightest form of matter which is known: its weight is only $\frac{1}{16}$th of that of an equal bulk of oxygen, and little more than $\frac{1}{15}$th of that of air: 100 cubic inches of it weigh but 2·14 grains. Owing to its levity, it has been extensively used for aërostatic purposes, although the facility with which coal gas can now be obtained has caused this latter, notwithstanding its much greater density, to be universally substituted for hydrogen in filling balloons. A light bag made of the craw of a turkey may easily be inflated with hydrogen, and will ascend rapidly, and carry with it a weight of several grains. Owing to the lightness of the gas, a jar may be easily filled with it by *displacement* without using the pneumatic trough:—A tube, 8 or 10 inches long, is fixed by a cork, in the manner shown at A, fig. 255, into a three-necked bottle containing some granulated zinc; diluted sulphuric acid is introduced through the funnel, and the gas, after the atmospheric air in the bottle has been allowed to escape, may be collected by holding a jar over the tube, as at B. The hydrogen will be retained for some minutes even if the jar be removed, provided that it be still held in the inverted position; while if the mouth be turned upwards, the gas will have escaped after the lapse of a few seconds. Hydrogen has a smaller combining number than any other elementary body, and it has hence been taken as the unit or standard of comparison. Its proportional number is therefore unity, or 1, and its combining volume 2, or double that of oxygen: the *combining volume* of a gas being the proportion in bulk in which it enters into combination with other gases, as compared with the bulk occupied by an equivalent quantity of oxygen, under similar circumstances of temperature and pressure. Pure hydrogen, though it cannot support life, is not poisonous, and when mixed with a certain proportion of oxygen it has been breathed for some time without inconvenience; but, owing to its rarity, it renders the voice temporarily much sharper and more shrill than usual.

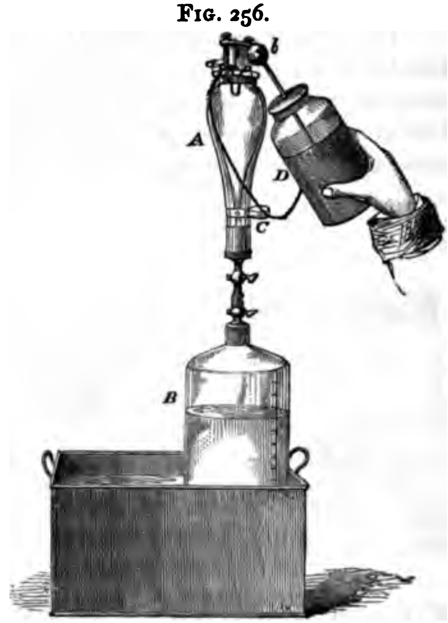
FIG. 255.

(294) *Synthesis of Water.*—Hydrogen is extremely inflammable; when a lighted taper is plunged into a jar of it, the gas takes fire, but the taper is extinguished. A jet of hydrogen burns with a pale yellowish feebly luminous flame, but gives out great heat. If the gas be dried by causing it to pass through a tube containing chloride of calcium, and a cold bell jar be held over

the burning jet, the interior of the glass quickly becomes bedewed with moisture, owing to the formation of water by the union of the burning hydrogen with the oxygen of the atmosphere. Oxygen and hydrogen may be kept in a state of mixture at the ordinary temperature of the air for an unlimited period without entering into combination; but the passage of an electric spark, the application of a lighted or even of a glowing match, and, in some instances, the mere contact of a cold metallic substance, such as platinum, especially if the metal be in a finely divided state (62), is sufficient to determine their immediate combination. Sudden compression of the gases, when mixed, produces the same effect from the heat evolved, whilst a still greater amount of compression if it be gradually applied, even when raised till it is equal to that of 150 atmospheres, fails to produce their union.

Cavendish, in his inquiries respecting the formation of water, effected the combination of the two gases by means of the electric spark. He employed for this purpose a strong glass vessel, a modification of which is represented at A, fig. 256. Through the upper part two platinum wires are inserted to within the eighth of an inch of each other. The vessel can be closed at the bottom by a glass stopcock, C. The air is exhausted, and the vessel screwed upon the top of a jar, B, containing a mixture of two measures of hydrogen and one measure of oxygen: on opening the stopcocks a portion of the mixture enters the vessel; the cocks are then closed, and an electric spark passed through the mixture by discharging a small Leyden jar, D, through the platinum wires, *a*, *b*.* A bright flash is seen at the moment of the discharge, and the gases combine, forming steam, which becomes condensed on the sides of the glass: the whole of the two gases, if mixed in the

FIG. 256.



* The discharge from the *secondary current* of a Ruhmkorff's coil may in all such *cases be advantageously substituted* for the spark of the Leyden jar.

above proportions, enter into combination with each other. On again opening the stopcocks a fresh quantity of the gases may be admitted, to supply the place of those just condensed, the spark may again be transmitted, and the process may be repeated till the whole of the gases are consumed, and a considerable quantity of water formed.

The uniformity of composition, and regularity of proportion in which compounds are produced when they combine chemically, is strikingly illustrated by means of a mixture of oxygen and hydrogen gases. The two gases may be mixed in any arbitrary proportion in a suitable vessel, into the sides of which two platinum wires are fused for the purpose of transmitting the electric spark. If the mixture be capable of exploding at all, the combination will be found to have occurred in the proportion of two measures of hydrogen to one measure of oxygen, no matter in what proportion the gases were mingled. If oxygen be used in excess, the superfluous oxygen will be found remaining uncombined; and if hydrogen be in excess, the excess of hydrogen will be left unaltered after the transmission of the spark.

Upon this principle a valuable instrument, the *Eudiometer*, is constructed, by means of which various gaseous mixtures may be analysed with great exactness. Many different forms of this instrument are in use. One of the simplest and most convenient consists of a stout siphon tube, fig. 257, open at one extremity and closed at the other. Into the sides of the tube, near the sealed end, two platinum wires, *a b*, are fused, for the purpose of transmitting an electric spark through the cavity of the tube. The sealed limb is accurately graduated to hundredths of a cubic inch, or other suitable divisions. Suppose it be desired to ascertain the proportion of oxygen in atmospheric air; the instrument is first filled with mercury, after which a small quantity of air is introduced: the bulk of this air is then accurately measured, taking care that the liquid stands at the same level in both tubes. A quantity of pure hydrogen about equal in bulk to the air is next introduced, and the bulk of the mixture is again accurately measured. The open extremity of the tube is now closed with the finger, below which a column of atmospheric air is safely

FIG. 257.

included; this portion of air acts as a spring which gradually checks the explosive force, when the combination is effected by passing a spark across the tube by means of the platinum wires. The gas is then exploded by the discharge of the Leyden jar. The remaining gas now occupies a smaller volume, owing to the condensation of the steam which has been formed. Mercury is therefore again poured into the open limb, until it stands at the same level in both tubes, and the volume of the gas is measured a third time. One-third of the reduction in bulk experienced by the gas will represent the entire volume of oxygen which the mixture contained. For delicate experiments, a very complete though expensive form of eudiometer upon this principle has been contrived by Regnault. (*Ann. de Chimie,* III. xxvi. 333.)

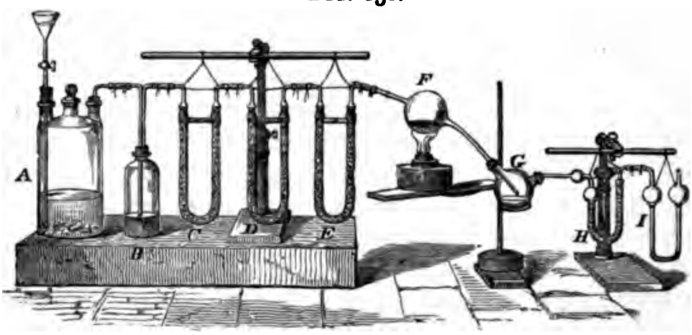
If a mixture of oxygen and hydrogen be fired in the air in considerable quantity, as when a bladder-full is ignited,—or, what is still better, when a quantity of soapsuds is blown up into a lather by forcing some of the gaseous mixture out of a bladder through a pipe under the liquid,—a loud and sharp report attends the combination; the steam formed suddenly expands from the high temperature attendant on the combustion, and immediately afterwards becomes condensed: great dilatation is first produced, followed by the formation of a partial vacuum; the surrounding air rushes in to fill the void, and by the collision of its particles produces the report. If the hydrogen be mixed with air, a similar but feebler explosion occurs when a lighted match is applied; hence it is especially necessary in all experiments with hydrogen to allow time for the expulsion of the atmospheric air from the apparatus before setting fire to the issuing jet. The explosion is most violent when 2 measures of hydrogen are mixed with 5 of air: if the mixture be diluted with a large excess either of hydrogen or of air, the explosion becomes more feeble; the heat evolved is less intense, and the combustion less sudden, until at a certain degree of dilution no explosion follows the application of flame, but the mixture burns slowly; whilst, if still more diluted, it takes fire only just at the spot where the heat is applied, but the combustion does not spread through the mass.

If a long tube, open at both ends, be held over a jet of burning hydrogen, a rapid current is produced through the tube which occasions a flickering in the flame, attended by a series of small explosions that succeed each other so rapidly and at such regular intervals as to give rise to a musical note, the pitch and quality of which varies with the length, thickness, and diameter of the tube.

Pure water may be *formed in considerable* quantities by a

method different from those hitherto described; the operation at the same time furnishes a means of ascertaining accurately the relative weights of oxygen and hydrogen which enter into the composition of water. It consists in transmitting a current of hydrogen over a weighed quantity of oxide of copper: at a red heat hydrogen deprives the oxide of copper of its oxygen, and forms water; by determining the weight of the water thus produced, and the loss sustained by the oxide of copper, the proportion of hydrogen which has combined with the oxygen can be ascertained. The apparatus

FIG. 258.



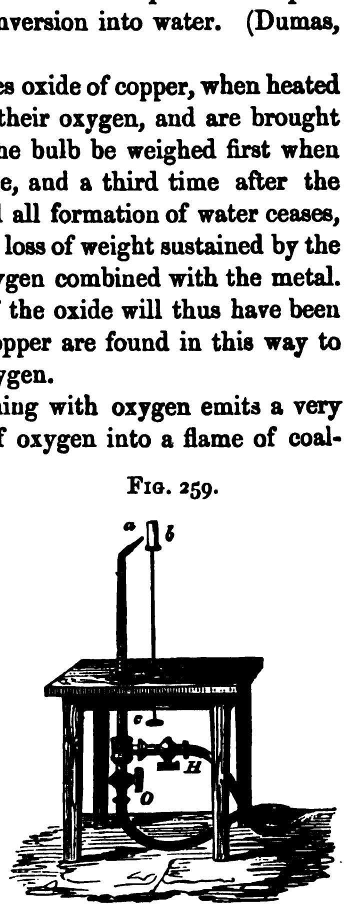
required for the purpose is represented in fig. 258. A quantity of oxide of copper is placed in the globe, F, which is constructed of glass of difficult fusibility, and the globe and its contents are accurately weighed after. A current of hydrogen, prepared from zinc and sulphuric acid in the bottle, A, is allowed to bubble up through a solution of potash, B, and to traverse three bent tubes in succession; the first, C, is filled with fragments of pumice-stone moistened with a solution of corrosive sublimate (HgCl); the second, D, contains fragments of fused caustic potash; and the third, E, is charged with pumice moistened with oil of vitriol. The mercurial salt and the potash remove the traces of arsenic, sulphur, and carburetted compounds, which the gas might otherwise carry over, and the oil of vitriol absorbs the last traces of moisture. Perfectly pure and dry hydrogen gas is thus delivered in the globe, F. When all the air is completely displaced, heat is applied to the globe; the oxide of copper gives up its oxygen; water is formed, and becomes condensed in the receiver, G, as well as in the attached bent tube, H, which is filled with fragments of pumice moistened with oil of vitriol: the whole of the water formed is by this means arrested. I is a bulb tube containing a little oil of vitriol, which prevents the entrance of extraneous moisture, and by its motion shows the progress of the gas. When

the globe, F, is cold, the hydrogen is displaced by a current of air, and on weighing the globe with the oxide after the experiment has terminated, the loss gives the quantity of oxygen which has combined with the hydrogen; whilst the difference between the amount of oxygen and that of the water condensed in the receiver, G, and tube of acid, H, shows the quantity of hydrogen that has combined with it. Each grain of hydrogen is in this manner proved to require exactly 8 grains of oxygen for its conversion into water. (Dumas, *Ann. de Chimie*, III. viii. 189.)

Many other metallic oxides besides oxide of copper, when heated in a current of hydrogen, part with their oxygen, and are brought back to the metallic condition. If the bulb be weighed first when empty, then when charged with oxide, and a third time after the stream of gas has been continued till all formation of water ceases, and till the tube has become cool, the loss of weight sustained by the oxide furnishes the proportion of oxygen combined with the metal. A true and very accurate analysis of the oxide will thus have been effected: 39·75 parts of oxide of copper are found in this way to contain 31·75 of copper and 8 of oxygen.

Hydrogen in the act of combining with oxygen emits a very intense heat. By throwing a jet of oxygen into a flame of coal-gas or of hydrogen, or still better by introducing a jet of oxygen, as at O, fig. 259, into the centre of a jet connected at H with a gas-holder supplying hydrogen, so that the two gases may become mixed just before they issue from the common orifice of the tube *a*, a heat may be obtained which can scarcely be surpassed. Sometimes the two gases are mixed in the proportion of 2 volumes of hydrogen to 1 volume of oxygen, and introduced into a bladder and burned as they issue through a tube of particular construction, known as Hemming's safety jet. It consists of a brass tube, about 6 inches long and two-thirds of an inch in diameter, filled with pieces of very fine brass wire, which are packed closely together, and then wedged in very tightly by driving a stout conical piece of wire into the axis of the tube (402). This tube is supplied at one extremity with a blowpipe jet, and at the other with a screw which can be connected with a stopcock adjusted to the neck of the

FIG. 259.



bladder. The temperature produced by burning the mixed gases from such a jet is so intense that thick platinum wire is melted by it with ease, and is partially volatilized; iron and steel are melted and burn with vivid scintillations. Rock crystal may be liquefied, and drawn out into threads like glass, and the stem of a tobacco pipe may be fused into an enamel-like bead. When the oxyhydrogen flame, which is but very feebly luminous, is directed upon a small cylinder of lime, *b*, this earth does not fuse, but it becomes white hot, and then emits a very pure white light of great steadiness and intensity, which may be maintained for hours, if care be taken to expose to the flame fresh surfaces of the lime by causing it to revolve by clockwork, continually but very slowly. This object may be obtained less perfectly by occasionally turning the pin, *c*, which supports the lime. Without this precaution a cavity would be formed opposite to the jet from volatilization of a small quantity of the lime. This light was originally proposed by Lieut. Drummond, to be used in the trigonometrical survey of Great Britain, and it is astonishing at what distances it may be seen when the rays are concentrated by a parabolic reflector. On the 31st December, 1845, it was seen across the Irish Channel, at half-past 3 P.M. (during daylight) from the top of Slieve Donard, in Ireland, by an observer stationed at the top of Snowdon,—an interval of 108 miles in a direct line; and it has more than once been seen at a distance of 112 miles.

Water is formed abundantly whenever combustible bodies which contain hydrogen are burned with a free supply of air. Wood, tallow, oil, wax, alcohol, coal gas, and most of our ordinary combustibles which burn with flame, in this manner furnish considerable quantities of water in the act of burning.

A striking experiment may be performed with hydrogen, which shows how purely conventional are the terms 'combustibles' and 'supporters of combustion.' Let a tall bottle with a narrow neck be filled with hydrogen gas; through a cork which passes easily into the neck of the bottle fit a jet connected with a gasholder containing oxygen; place the bottle mouth downwards and set fire to the hydrogen, then immediately insert the cork and jet, through which a stream of oxygen is gently issuing. The flame will appear to attach itself to the oxygen tube, and the jet of oxygen will be burning in an atmosphere of hydrogen. Combustion, in fact, occurs at the place where the two gases first come into contact. Suppose, for a moment, that the earth's atmosphere had contained hydrogen instead of oxygen; oxygen would have appeared to us in the light of a combustible gas, and hydrogen in that of a supporter of combustion.

CHAPTER IV.

CARBON—CARBONIC ACID—CARBONIC OXIDE.

§ I. Carbonic Acid ($CO_2 = 22$); *Comb. Vol.*, 2; *Sp. Gr.*, 1·529.*

(295) An atmosphere composed only of oxygen, nitrogen, and steam, though perfectly adapted to the support of animal life, would be unfit to sustain vegetation. Plants require for their growth and development a certain proportion of another gas—carbonic acid. Evidence of the existence of this body in the air (290 *b*) is easily obtained by exposing a saucer of lime water to the atmosphere: in a few minutes its surface becomes covered with a thin pellicle, which if disturbed by agitation sinks to the bottom. The pellicle is renewed after each agitation until the whole of the lime contained in the liquid has been thus rendered insoluble. This white matter is chalk, which is a compound of carbonic acid and lime. Such compounds of carbonic acid with bases are termed *carbonates*, hence chalk is chemically termed *carbonate of lime*. When the chalk thus obtained is heated to bright redness (which, if the result is to be accurately examined, must be effected in a platinum tube), carbonic acid is expelled as a colourless and transparent gas, while pure quick lime is left behind.

Preparation.—In actual practice carbonic acid is obtained by a much more convenient plan. Carbonic acid being but a feeble acid, is expelled from its compounds by almost every other acid which is freely soluble in water; it is therefore easily separated from its compounds by the addition of one of these acids. Fragments of chalk, or marble which is a more compact form of carbonate of lime, are placed in a retort or gas-bottle, and some powerful acid, such as the nitric or the hydrochloric, diluted with 8 or 10 times its bulk of water, is poured upon the chalk, when the acid seizes the lime and displaces the carbonic acid, which escapes with a violent effervescence. The following diagram shows the nature of this decomposition when chalk and nitric acid are employed:—

* If Gerhardt's formula for carbon and oxygen be adopted ($C=12$, $O=16$), carbonic acid will be represented as CO_2 with a combining number 44, and the acid must be regarded as *dibasic*.

Decomposition of Chalk by Nitric Acid.

Before decomposition.		After decomposition.
50 = 1 eq. of chalk (CaO, CO_2)	22 = 1 eq. Carbonic acid, (CO_2)	set free.
	28 = 1 eq. Lime (CaO)	82 = 1 eq. Nitrate of lime, (CaO, NO_5)
63 = 1 eq. hyd. nitric acid (HO, NO_5)	54 = 1 eq. Nitric acid (NO_5)	
	9 = 1 eq. Water (HO)	set free.

Or in Symbols; $CaO, CO_2 + HO,NO_5 = CaO, NO_5 + CO_2 + HO$.

Limestone, Iceland spar, oyster shells, pearlash, and carbonate of soda, all yield carbonic acid when acted on by a stronger acid.

Properties.—Under atmospheric temperatures carbonic acid is a colourless transparent gas, with a faintly acidulous smell and taste; but when generated in a confined space in strong vessels it becomes condensed to a liquid as transparent and colourless as water, which, according to Regnault, boils at —109°. At 32° F. it requires a pressure of 38·5 atmospheres to retain it in the liquid state (Faraday). It then has a specific gravity of 0·83, whilst at 86° the specific gravity is only 0·60. If these data be correct, the liquid expands by the application of heat four times more rapidly than air (Thilorier); but according to Andreeff (Liebig's *Ann.*, cx. 10) the expansion of the liquid, although greater than that of the gas, is not so great as Thilorier states. Andreeff found the density of the liquid 0·947 at 32°; 0·893 at 50°; 0·86 at 60°; and 0·779 at 78°. Liquefied carbonic acid does not mix freely with water, or with the fixed oils; but it is dissolved in all proportions by alcohol, ether, oil of turpentine, naphtha, and bisulphide of carbon. When a stream of the liquefied acid is allowed to escape into the air, it freezes into a snow-white solid (182): and if a tube containing liquid carbonic acid be plunged into a bath of the solid acid mixed with ether, and placed in the vacuum of the air-pump, the liquid acid in the tube will speedily be frozen into a clear transparent ice-like mass, which melts at —70°. The solidified acid is heavier than the liquid portion in which it is being formed.

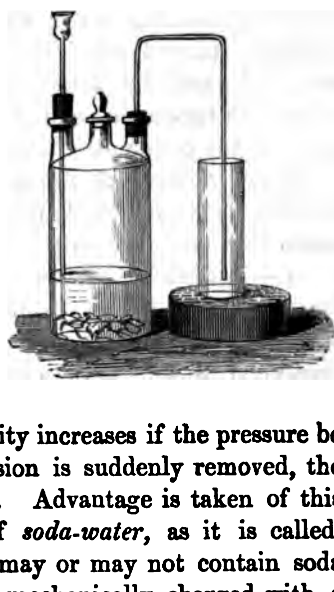
Carbonic acid gas is not inflammable, neither will it support the flame of burning bodies; the extinction of a taper is one of the means frequently resorted to for detecting its presence. Many other gases, however, have the same property; some additional test, therefore, becomes necessary. Such a test is afforded by its action upon lime-water, which, when agitated with the gas, is immediately rendered milky from the formation of chalk; a few drops of any strong acid dissolve the chalk and restore trans-

parency to the liquid; an excess of even carbonic acid has the same effect.

Carbonic acid gas in its concentrated form is irrespirable, for by producing spasm of the glottis it is prevented from entering the lungs; when diluted with air, however, it may be breathed without even a suspicion of its presence. If the proportion exceed 3 or 4 per cent. of the air it acts as a narcotic poison; and even in much smaller quantities its depressing effects are very injurious. The ill effects experienced in crowded and ill-ventilated rooms are chiefly due to the presence of this gas in undue quantity, and it is this circumstance which renders attention to ventilation a matter of such high importance.

Carbonic acid gas is more than half as heavy again as atmospheric air; 100 cubic inches of it at 60° F. and 30 inches Bar. weigh 47·303 grains; from its density it may easily be collected in dry vessels by displacement, in the manner represented in fig. 260, and may be poured from one vessel into another like water.

FIG. 260.



No definite hydrate of carbonic acid is known; the compound, both in the form of gas and in its denser conditions of liquid and solid, being anhydrous; so that it would be correct to speak of carbonic acid gas as *carbonic anhydride*. At the ordinary temperature, water may be made to take up about its own bulk of carbonic acid, and its solubility increases if the pressure be increased;* but when the compression is suddenly removed, the gas escapes with brisk effervescence. Advantage is taken of this circumstance in the preparation of *soda-water*, as it is called. For this purpose the water, which may or may not contain soda or other substances in solution, is mechanically charged with a large quantity of carbonic acid gas, by the use of a condensing syringe, attached to a reservoir filled with the gas. The excess of the gas thus forced into the liquid occasions the agreeable briskness and pungency so much prized in this beverage. A solution of carbonic acid in water reddens tincture of litmus; but the red colour disappears if the liquid be boiled for a few minutes,

* If the gas be simply transmitted through the water, the liquid seldom takes up more than two-thirds of its bulk.

owing to the expulsion of the gas. The aqueous solution of the acid possesses solvent powers which, though in many instances extremely feeble, are yet far more extensive than those of pure water. By the continuous action of water charged with carbonic acid, even granite and the hardest rocks are disintegrated, few finely divided minerals being able to resist its gradual and long continued action. The proportion of gas dissolved is in many instances very minute, but as few natural sources of water exist which are not to a greater or less extent impregnated with carbonic acid, either by absorption from the atmosphere or from the soil, the solution, insignificant as it may at first sight appear, is continually proceeding, and in the lapse of time it effects changes of great importance and extent.

The briskness of spring water is partly due to the carbonic acid which it contains; though its usual coolness and the abundance of atmospheric air dissolved in it are still more important. It is the absence of these qualities which renders boiled or distilled water flat and insipid. Carbonic acid was originally termed *fixed air*, from the circumstance of its having been discovered by Dr. Black in 1757, as a solid or fixed constituent in limestone, and from its becoming fixed or absorbed, by solutions of the pure alkalies.

(296) *Sources of Carbonic Acid.*—Besides the processes of procuring the gas already described, there are a variety of cases in which it is produced on a very large scale in nature.

1.—Respiration in man and animals is always attended with the formation of a large proportion of the gas. This fact may be easily proved by forcing air from the lungs by means of a tube through lime-water, which will speedily become milky from the deposition of carbonate of lime. The proportion of carbonic acid in respired air varies from 3 to 4 per cent., being usually about $3\frac{1}{2}$ per cent.

2.—Carbonic acid is also abundantly disengaged in the process of fermentation, and is the cause of the briskness of bottled beer, champagne, and other fermenting liquors. Many accidents have occurred from persons incautiously descending into an empty fermenting-vat before the gas has had time to escape and mix with the air; it is usual to facilitate the escape of the dense gas by leaving the plug at the bottom of the vessel open for some hours.

3.—In the operation of burning lime in the lime-kiln, the heat expels from the limestone the carbonic acid, which escapes in large volumes. Many a poor houseless wanderer, tempted by the warmth of the kiln, has lain down in the stream of air proceeding from it, and has slept to wake no more. By the operation of subterranean heat in volcanic districts upon limestone

beneath the surface, large volumes of carbonic acid are continually finding their way into the atmosphere; immense quantities are discharged from open craters or from fissures and cavities in the soil; the springs in such districts are also frequently highly charged with it, and the gas escapes with effervescence when they reach the surface. The springs of Seltzer, Pyrmont, and Marienbad, on the Continent, and of Tunbridge, in our own country, exhibit this phenomenon.

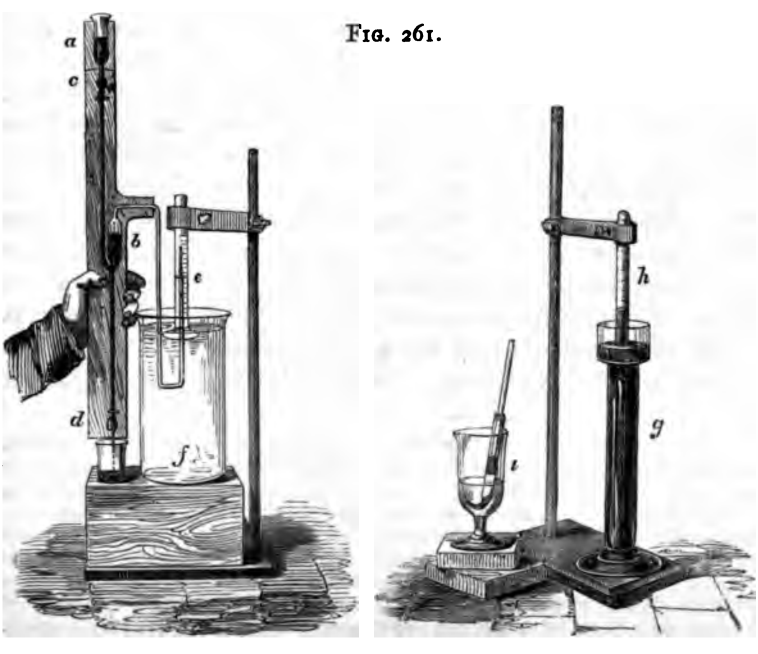
4.—The carbonic acid met with in spring water is in many instances derived from the gradual oxidation of the vegetable and other organic matter which it holds in solution, by the action of the oxygen of the air which all waters naturally contain. The lake waters from the primitive districts, such as those in the northern parts of Scotland, leave scarcely any residue on evaporation except a little organic matter; they are very free from carbonic acid, and the bulk of oxygen held in solution is somewhat more than one half that of the nitrogen. If such waters be kept in closed vessels for a few weeks in a warm room, the oxygen gradually decreases, and in its place a corresponding volume of carbonic acid is found. The pure water of Loch Katrine, for example, when first collected did not contain more than 0·06 cubic inches of carbonic acid per gallon; but the quantity of this gas which the same sample contained after it had been kept in a closed vessel for some weeks, in a warm room, rose to 0·38 cubic inches in the gallon, whilst the oxygen had diminished to a similar extent. Spring waters which rise in a sandy district, the surface of which is sparingly clothed with vegetation, and from which consequently they can take up but little organic matter, contain but small quantities, often mere traces, of carbonic acid; whilst the springs of highly cultivated districts, such as those which rest more or less directly upon the chalk, become charged with organic matter, which gradually undergoes oxidation in the soil, and the quantity of carbonic acid contained in such waters is always considerable, whilst the quantity of oxygen is proportionately reduced.* The extent to which this change takes place in

* The analysis of these gases or of any mixture of air with carbonic acid, such, for example, as respired air, may be effected with sufficient accuracy for most purposes, in the following manner:—Supposing that the gas had been collected over either water or mercury, it becomes necessary to transfer a portion of it from the jar in which it has been collected to the one in which it is to be analysed. A method of effecting this is shown in fig. 261. Upon the board, *a d*, is fastened a pipette, designed for effecting this transfer; *a* is a cylindrical funnel of a capacity of about two cubic inches; at *c* is a small steel stopcock, or a piece of vulcanized caoutchouc tubing compressed by a screw, which is simpler and less expensive; by either of these contrivances the contents of the funnel can be admitted to a wide thermometer tube, which is

river water is very remarkable. It is well exhibited in the case of the Thames. On one occasion, some samples were taken from the river at low water at different points on the same day, in August, 1859; those collected above the metropolis being nearly

furnished at *d* with a second steel stopcock or caoutchouc tube and screw clamp; *b* is a bulb of the capacity of one cubic inch, or rather less; from the upper part of *b* proceeds another piece of thermometer tube, bent as shown in the figure, to allow of its introduction into the gas-jar. To use the instrument, the funnel, *a*, is filled with mercury, the stopcocks are both opened, and as soon as the air has been displaced from the vertical portion of the fine tube, and mercury escapes through *d*, the stopcock *d* is closed; the mercury quickly displaces the air from the rest of the tube, and from the bulb, *b*, and as soon as it begins to flow out at the open extremity of the recurved portion, the stopcock, *c*, is closed. The instrument being now full of mercury, is introduced into the jar, *e*, of the gas to be transferred, and its open extremity is raised above the level of the water in the jar, *e*; the stopcock, *d*, is then opened, and whilst the mercury runs out into a vessel placed for its reception, the gas enters from *e*, and occupies the place of the mercury in the bulb, *b*. When a sufficient quantity has been admitted, the tube is depressed below the level of the water in the jar, *e*; the stopcock, *d*, is closed, and the pipette, which is sealed by the admission of a little water into the capillary tube, is withdrawn from the jar, *f*. The gas can now be transferred to the graduated tube, *h*, standing in the jar of mercury, *g*; the bent limb of the pipette is introduced into the tube, *h*, which has been previously filled with mercury. Fresh mercury is poured into the funnel, *a*, of the pipette, and on opening the stopcock, *c*, the gas is expelled into the tube, *h*; the gas should not occupy more than two-thirds of the capacity of this tube.

FIG. 261.



The proportions of carbonic acid, of nitrogen and of oxygen, are now easily

free from contamination with sewerage products, whilst those obtained lower down were extensively impregnated with them. The gases were expelled from each sample by boiling, within twenty-four hours of the time of its collection, and the results obtained are given in the following table, in which they are contrasted with the proportions of each gas furnished by a similar experiment upon a sample of river water taken above Teddington Lock, where it was in a pure condition.

Temp. of river, 71°	Kingston.	Hammer-smith.	Somerset House.	Greenwich.	Woolwich.	Erith.
Total quantity of gas in cubic in. per gallon	14·67	Not deter-mined.	17·49	19·77	17·50	20·64
Carbonic Acid . . .	8·42	Not deter-mined.	12·56	15·42	13·40	15·80
Oxygen	2·07	1·16	0·43	0·07	0·07	0·52
Nitrogen	4·18	4·24	4·50	4·28	4·03	4·32
Proportion of Oxygen to Nitrogen . . .	1 : 2	1 : 3·7	1 : 10·5	1 : 60	1 : 52	1 : 8·1

From these experiments, it will be seen that the water from Kingston (above Teddington) is thoroughly aërated, and contains oxygen in the proper proportion to the nitrogen. At Hammersmith, the effect of the organic impurities in abstracting the oxygen begins to be evident. It is much more marked at Somerset House, whilst at Greenwich, where the condition of the river at low water is about at the worst, the oxygen has nearly disappeared.

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ascertained in the following manner:—The bulk of the gas in the tube, *h*, is to be carefully read off, care being taken to bring the mercury to the same level within and without the tube; the temperature and the pressure being observed as usual. Supposing that it has thus been ascertained that a bulk of gas of about two-thirds of a cubic inch is to be subjected to the analysis, the operator, by means of a glass syringe, throws up ten or twelve drops of a solution of caustic potash (sp. gr. 1·4) into the tube. The glass syringe may be extemporaneously prepared from a strong tube which is softened in the flame of a lamp, drawn off and recurved at one end, as shown in the figure at *i*; this constitutes the body of the syringe, whilst the piston is easily formed of a piece of glass rod, provided with a plug of caoutchouc.

The operator then agitates the contents of the tube by rapidly thrusting down the tube into the mercury, and withdrawing it, taking care to keep the mouth below the surface of the mercury: this manœuvre is several times repeated in quick succession; the tube is again left at rest for a minute or two, and the absorption is noted by a second time reading off the volume of the gas at the proper level. The difference indicates the amount of carbonic acid.

In order to ascertain the proportion of oxygen in the remainder, the plan recommended by Liebig is the simplest:—a solution of 1 part of pyrogallic acid in 6 of water is prepared, and about 40 drops of the solution is by a *fresh* syringe injected into the tube *h*, and the mixture is briskly agitated as before; the solution of potash, if oxygen be present, becomes of an intense bistre colour, and the oxygen is quickly and completely absorbed; the gas is measured a third time, and the residue is estimated as nitrogen; the difference between the second and third readings giving the volume of oxygen.

At Woolwich, it is nearly as bad, but by the time Erith is reached, a great improvement is perceptible. Had the experiments been continued still lower down the river, the proportion of oxygen would have continued to increase, owing to the admixture of aërated sea-water and the absorption of oxygen due to the successive exposure of the water to the air in its onward flow.

5.—Carbonic acid constitutes what is termed *choke-damp* by miners, and it often occasions much loss of life after the occurrence of an explosion of carburetted hydrogen, or *fire-damp*. It frequently also accumulates in the old workings of mines, and in pits or wells. Before descending into them, it is usual to lower a candle in order to ascertain whether the light will burn; if it does so, it is generally considered safe to venture down. Instances, however, are on record in which a candle was found burning in an atmosphere which, notwithstanding, contained sufficient carbonic acid to cause death. When it is necessary to enter into an atmosphere considerably charged with this gas, Graham suggests as a precaution that the mouth and nostrils be covered with a cloth containing a mixture of slaked lime and crystallized sulphate of soda. Such a mixture is porous enough, in a layer of an inch thick, to allow the passage of sufficient air for respiration, whilst the moist lime completely absorbs the carbonic acid.

6.—There is also another mode in which carbonic acid is very largely formed, which, independently of its importance as a source of the gas, is interesting as throwing light upon its chemical nature. Whenever charcoal, or bodies which, like wood, coal, oil, or tallow, contain charcoal, are burned either in oxygen or in air, carbonic acid is obtained abundantly; if the gas, after combustion has terminated, be agitated with lime water, the liquid will be immediately rendered milky.

Carbon may again be extracted from carbonic acid. If a small piece of potassium, heated till it begins to burn in air, be introduced by means of a platinum spoon into a jar of dry carbonic acid gas, the potassium will continue to burn with great brilliancy. Potash will be formed at the expense of the oxygen which the gas contains, whilst charcoal is liberated, as may be seen in the black particles which are suspended in the water into which the spoon is plunged after the combustion is complete. Thus carbonic acid is shown, both synthetically and analytically, to be a compound substance, consisting of charcoal and oxygen, and its composition may be represented as follows:—

		By weight.		Dumas.	By vol.			Sp. gr.
Carbon	C =	6	or 27·28	27·28	2	or 1·0?	=	0·4146
Oxygen	O_2 =	16	72·72	72·72	2	1·0	=	1·1057
Carb. acid	CO_2 =	22	100·00	100·00	2	1·0	=	1·5203

Carbonic acid is not decomposed by mere elevation of temperature, but if a succession of electric sparks be transmitted through the gas it is partially separated into carbonic oxide, and free oxygen. Sulphur, chlorine, and the halogens may be heated with the gas without decomposing it; but if heated with hydrogen, water and carbonic oxide are formed, the decomposition being represented thus, $CO_2 + H = CO + HO$. Carbon, and many of the metals, such as iron and zinc, also remove a portion of the oxygen from the carbonic acid, and convert it into carbonic oxide (303).

Applications.—Mr. Goldsworthy Gurney has turned the property of extinguishing flame possessed by carbonic acid to an important practical account. Coal mines, at different times and from various causes, are liable to take fire, and from the vast mass of heated matter, the conflagration not unfrequently resists all the ordinary means of checking its ravages; many acres of subterranean fire are thus produced, and the workings are of necessity abandoned. Mr. Gurney, in such cases, closes every opening into the mine but two, one for the entrance, the other for the escape of the gases, and then, by the agency of the steam jet, pours into the mine a current of impure carbonic acid and nitrogen, obtained by forcing a stream of air through a coke furnace into the mine, so as to fill the entire workings with the gas; he has thus on several occasions succeeded at a very small expense in extinguishing fires which have raged unsubdued for years. A very remarkable case of this kind was mentioned in the *Times* for May 22, 1851:—The 'burning waste of Clackmannan,' situate about seven miles from Stirling, had been for 30 years on fire. It occurred in a seam of nine-foot coal, and extended over an area of 26 acres; yet the fire was successfully extinguished:—about 8,000,000 cubic feet of gas were required to fill the mine, and a continuous stream of impure carbonic acid was kept up night and day for about three weeks. The difficulty lay not so much in putting out the fire, as in cooling down the ignited mass so that it should not again burst into flame on readmitting the air. In order to effect the necessary reduction of the temperature, water was blown in along with the carbonic acid in the form of a fine spray or mist. Subsequently, cold air mixed with the spray was blown in, and in a month from the commencement of operations the fire was found to be completely extinguished.

Carbonates.—Though but a feeble acid, the carbonic acid unites with the metallic protoxides, and forms a numerous and important class of salts, which have hitherto been generally regarded as monobasic; in which case they would contain one equivalent of the acid to one equivalent of the base, like carbonate of lime (CaO,CO_2). But in the case of the alkalies a second equivalent of carbonic acid may be combined with the metallic oxide; thus with potash there is a carbonate (KO, CO_2), and a bicarbonate or acid carbonate ($KO, HO, 2\ CO_2$).* The carbonates, with the exception of those of the alkalies, are not soluble in water, but many of these insoluble carbonates, and in particular those of lime, magnesia, baryta, and strontia, may be dissolved to some extent by water charged with carbonic acid, and are deposited in a crystalline form as the gas slowly escapes from the liquid. All the carbonates are dissolved with effervescence by diluted nitric acid, and even by acetic acid: the gas which comes off is colourless, and renders lime water turbid; it possesses the properties of carbonic acid, above described. The most delicate test of the presence of free carbonic acid is one of the basic salts of lead, such as the subnitrate or the subacetate, a solution of which is instantly rendered milky by the action of carbonic acid gas upon it. The alkaline carbonates, when in solution, are also decomposed by acids, with effervescence; they give with salts of lime a white precipitate, which is immediately re-dissolved by an acid, with effervescence. All the carbonates, with the exception of those of potash, soda, and baryta, are decomposed by prolonged ignition, the acid being entirely expelled from the salt. The carbonates have considerable tendency to combine with each other, and form double salts, like dolomite, which is a double carbonate of lime and magnesia ($MgO, CaO, 2CO_2$). Many basic carbonates are also known; they sometimes contain 2 atoms of base to one atom of the acid, and are often hydrated compounds—such, for example, as malachite ($2\ CuO, HO, CO_2$).

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* Owing to the existence of these salts, conjoined with a consideration of the properties of many of the compounds which carbonic acid forms with certain organic substances, this acid is now very generally regarded as dibasic (460) in which case its formula would be C_2O_4, or double of that formerly adopted; carbonate of lime would then be represented as $2CaO, C_2O_4$; carbonate of potash as $2KO, C_2O_4$; and bicarbonate or the acid carbonate of potash, as KO, HO, C_2O_4. The formulæ of all the carbonates hitherto regarded as neutral would, upon this view, be doubled, while those of the acid carbonates and double carbonates would retain their former value unchanged. The strongest arguments in favour of doubling the formula of carbonic acid are, however, derived from the phenomena of organic chemistry, and consequently they cannot be advantageously discussed at this point; we shall for the present continue to indicate the carbonates by the simpler formula as salts of a monobasic acid, in accordance with long-established usage..

§ II. Carbon. ($C=6.$)*

Sp. Gr., as diamond, 3·33 to 3·55; *Theoretical Density of its Vapour,* 0·4146; *Comb. Vol.,* 2.

(297) Carbon is an elementary body of the greatest importance. It is found nearly in a state of purity in the diamond; with a larger proportion of foreign admixture it occurs in the form of graphite, and still less pure in the abundant deposits of pit coal. It is also met with in enormous quantities in combination, under a variety of forms. Independently of the quantity of it which exists diffused through the atmosphere in the state of carbonic acid, it is a component of the numerous varieties of carbonate of lime and of magnesia, constituting nearly an eighth of the entire weight of the former, and more than a seventh of that of carbonate of magnesia. It is the characteristic ingredient of all substances which are termed *organic*; that is, of substances which are produced directly or indirectly from the vegetable or animal creation. The solid parts of plants, shrubs, and trees owe their form and solidity to this element, which is mainly supplied to them from the carbonic acid in the atmosphere. This action of plants upon carbonic acid is one of the means ordained for preserving uniformity in the composition of the air. The quantities of carbonic acid poured forth from the bowels of the earth, and derived from the processes of respiration and combustion, and from numerous other less apparent sources, would by degrees occasion an injurious accumulation of the gas, but for this compensating action. In solar light the leaves of plants decompose both carbonic acid and water, appropriating the carbon and the hydrogen of each for their own growth and nutrition, whilst a large proportion of the oxygen which these compounds contained is returned into the air in the gaseous state. The carbonic acid thus poured out by animals as a refuse and poisonous product, supplies food and sustenance to the vegetable world, which in its turn converts the carbon into a form suitable for the maintenance of life in animals. Each great division of animated nature is thus seen to be essential to the well-being and even to the support of the other. The fuel which has been burned and dissipated in vapour, is again reduced to the solid state, and by the agency of vegetable life, it is once more fitted for combustion. Plants are in fact the grand agents by which deoxidation is effected,

* Gerhardt doubles the atomic weight of carbon, making $C=12$, and the arguments in favour of this are so strong, that, but for the confusion which would be introduced into our chemical notation, it is probable that few chemists would hesitate to adopt the suggestion.

while animals are the channels through which re-combination with oxygen is unceasingly produced.

(298) *Diamond* (C_a), *Sp. Gr.*, from 3·33 to 3·55.—Carbon is found in its purest state in the *diamond*, in which it occurs crystallized in forms belonging to the regular system. The crystals are generally derivatives from the octohedron, with a cleavage parallel to each of the planes of the octohedron; the faces are often convex, and the edges are generally rounded, or *lenticular*, as they are termed in such crystals. Diamonds usually present themselves under the appearance of semi-transparent rounded pebbles, enclosed in a thin brownish opaque crust. The gem, when freed from this coating, is generally colourless; such specimens are the most prized; it is, however, met with of various tints, the more common of which are yellow and different shades of brown. The most famous diamond mines are those of Golconda and Bundelcund, in India, of Borneo, and of the Brazils. The origin of the diamond is entirely unknown; it is not probable that it has been formed by crystallization after fusion, since intense heat reduces the diamond to the form of graphite. The circumstances under which diamonds are found in nature afford no clue to the process of their formation. In the year 1827, a diamond was found imbedded in a fine-grained quartzose rock (*Itacolumite*) in Brazil, but with few exceptions the gem is found scantily in an alluvial matrix, consisting chiefly of sandstone and rolled quartz pebbles, from which the diamonds are extracted by washing and careful sorting.

Diamond is the hardest body known, crystallized boron approaching it most nearly in this respect: it is cut and polished by employing its own powder for the purpose. The fine diamond dust used for this object is mixed with a little olive oil, and spread over a revolving steel plate, and the diamond, cemented into a suitable support, has each of its faces in turn presented to the flat face of the disk.* The most important use to which the diamond is applied is the cutting of sheets of glass: only the natural face of the crystal can be employed for this purpose, crystals with curved faces being the best; they are set in a convenient handle, and a line in the proper direction is traced with the diamond across the glass;

* The Kohinoor diamond, which was cut in 1852, for the Queen, was imbedded in a copper vessel of about the size of a teacup, into which it was cemented with a mixture of equal parts of tin and lead. When it was necessary to change the position of the gem, the solder was melted by immersing the cup, with the diamond imbedded, in a charcoal fire, and heating the metal till it assumed a consistence resembling that of wet sand; in order to cool the diamond more quickly, it was plunged into warm water and then into cold water; the cutting was effected by means of a cast-iron wheel revolving on a

slight pressure on each side of the cut then determines the fracture in the right direction. A true cut is effected by such a diamond if properly used, whilst a diamond with angles obtained by cleavage produces only a superficial scratch with ragged edges (Wollaston, *Phil. Trans.*, 1816).

The diamond has a very brilliant lustre and a high refracting power; it is a non-conductor of electricity. After exposure to sunshine, many specimens emit a feeble phosphorescent light, which may be seen in a darkened room. In vessels from which air is excluded, it may be heated intensely without change. If it be suspended in a cage of platinum wire, heated to bright redness, and plunged into oxygen gas, it will burn with a steady red light, and with the production of pure carbonic acid. The diamond, however, is not perfectly pure carbon: it always leaves a minute yellowish ash, which has been found to contain silica and oxide of iron. This ash has generally the form of a cellular network, and may perhaps, at some future time, assist in determining the origin of this valuable gem. No heat hitherto applied suffices for the fusion or volatilization of the diamond, or indeed of carbon in any of its forms, though in the intense heat of the voltaic arc, it appears to be mechanically transported from one electrode to the other (301). When the diamond is introduced into the flame of the voltaic arc it undergoes a remarkable change; as soon as it becomes white hot it begins to swell up, loses its transparency, suddenly acquires the power of conducting electricity, becomes specifically lighter, and is converted into a black opaque mass, resembling coke. The density of a diamond thus altered, was 2·6778, while in its crystalline condition it was 3·336 (Jacquelain, *Ann. de Chimie*, III. xx. 467). The heat of the oxyhydrogen jet was found to be insufficient to produce this change.

(299) *Graphite, or Plumbago,* (C_β, *Sp. Gr.* from 2·35 to 2·15) is a second form in which carbon occurs native. Its most celebrated mine is situated at Borrowdale, in Cumberland, but it is also found in Ceylon, and in several parts of the United States, always in rocks belonging to the earliest formation: the Borrowdale graphite occurs in clay-slate; in other localities it is imbedded in gneiss, mica-slate, or granular limestone. Graphite occurs either massive or in six-sided crystalline plates belonging to the rhombohedral

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vertical axis about 2400 times per minute; the diamond rested upon the upper surface of the wheel, being held in its position by a kind of vice, and the pressure against the revolving disk was increased or diminished by adding or removing weights. From time to time the face of the diamond was touched with a hair pencil dipped in a cream of diamond *dust and oil.*

system. Carbon, in the two forms of diamond and plumbago, offers an excellent instance of dimorphism; the properties which it displays in these two states are as widely different as those of any two dissimilar elements. Graphite has a metallic, leaden-grey lustre, whence its familiar name of *black-lead.* It is very friable, and consequently feels unctuous to the touch, and leaves traces on paper upon which it is rubbed. The particles of which it is composed are, however, extremely hard, and they rapidly wear out the saws employed to cut it. It appears to exist in two distinct modifications, one of which, like the Borrowdale graphite, is fine-grained and amorphous; the other, like the Ceylon variety, is composed of small flat plates, united by a cementing material; this form of graphite generally occurs in a matrix of quartz (Brodie). Graphite is an excellent conductor of electricity. It is never met with in a state free from foreign admixture: when burned in oxygen it leaves from 2 to 5 per cent. of ash, which generally contains quartz, and oxides of manganese and iron; these bodies, however, are merely accidental impurities. The fine-grained amorphous graphite is highly prized for the manufacture of 'lead pencils': where pieces of sufficient size can be obtained they are sawed into thin slices, and these again into small rectangular prisms, which are placed in cedar wood for use. It has been found that the smallest fragments, if of good quality, and the fine powder (which was formerly consolidated by melting it with a minute quantity of sulphur, and was used for the coarser kinds of pencils) may be again reduced into coherent plates by subjecting it to enormous pressure, and may thus be fitted for the manufacture of the best pencils. Black-lead is extensively used for lubricating machinery, and as it is quite unaltered by exposure to the weather, it forms a useful coating to protect coarse iron work from rust. An application of graphite which is of some importance to the chemist, is its use in the manufacture of what are termed black-lead crucibles, or blue-pots: the clay used in making them is mixed with a coarse kind of graphite; the pots made from this mixture are much less likely to crack when heated than if made of fire-clay only.

Brodie (*Ann. de Chimie,* III. xlv. 351) has described a method of obtaining graphite in a state of purity, and in a very finely divided form. It consists in mixing coarsely-powdered graphite with a fourteenth of its weight of chlorate of potash; the mixture is introduced into an iron pot, and diffused through a quantity of concentrated sulphuric acid, equal to twice the weight of the graphite employed. The mixture is heated over a steam bath so long as any peroxide of chlorine is disengaged: it is then allowed to cool,

thrown into water, and washed thoroughly. If graphite which has been subjected to this treatment and dried, be heated to redness, it gives off gas, increases greatly in bulk, and becomes reduced to an exceedingly fine powder. In cases in which the graphite was originally mixed with silica, this impurity may be got rid of by adding a small quantity of fluoride of sodium to the mixture of graphite with chlorate of potash and sulphuric acid; the silica is then expelled in the form of fluoride of silicon (617).

It appears that during this process the graphite becomes oxidized; and that a new compound of carbon, hydrogen, and oxygen is formed, which enters into combination with the sulphuric acid,* and this compound is decomposed by ignition.

The graphitic modification of carbon may be obtained artificially by several processes. When cast iron is melted in contact with an excess of charcoal, it takes up a considerable quantity of it, and if the iron be allowed to cool slowly, the carbon crystallizes out in the six-sided plates peculiar to graphite. In the manufacture of coal-gas, those parts of the retort which are exposed to the highest temperature, partially decompose the gas as it escapes; a part of

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* This oxidized substance may be obtained in a state of purity by the following process (*Q. J. Chem. Soc.*, xii. 261):—Mix intimately 1 part of finely powdered Ceylon graphite with three parts of chlorate of potash, and add sufficient of the strongest nitric acid to render the mixture fluid; after which expose it for three or four days to the heat of 140° on a water bath. The direct action of solar light abridges the time required. The residue must be washed with water freely, dried, and subjected four or five times to the same treatment.

Graphic Acid ($C_{22}H_4O_{10}$), as this compound is termed by Brodie, forms yellow silky plates, which are insoluble in water and in acids. It is slowly attacked by ammonia and by potash, the ammonia gradually combining with it, forming a gelatinous body susceptible of decomposition by acids, which occasion the separation of a white gelatinous mass.

When graphic acid is exposed to a temperature of between 500° and 600°, it undergoes decomposition with almost explosive violence, with evolution of heat and light, giving off gas, and producing an exceedingly bulky, flocculent, sooty-looking substance which still retains both carbon and hydrogen. If, in order to regulate the heat applied, the graphic acid be placed in paraffin oil, and the temperature be gradually raised to 520°, the hydrocarbon becomes of a deep red colour, and the acid gives off water and carbonic acid, leaving a substance of graphitoid appearance, consisting of $C_{44}H_2O_8$; if this new body be further heated in an atmosphere of nitrogen, water and carbonic oxide escape, leaving a residue containing $C_{13}H_{24}O_{22}$. Even if heated to redness in nitrogen, it retains a portion of oxygen and hydrogen, giving off water, carbonic acid, and carbonic oxide.

Brodie considers that in these compounds the graphite retains its allotropic state, which he terms *Graphon*, and that it possesses in this form a combining number of 33, with the symbol Gr. If this be so, graphic acid $C_{22}H_4O_{10}$ might be represented as $Gr_4H_4O_{10}$, the first residue $C_{44}H_2O_8$ as $Gr_8H_2O_8$, and the second $C_{132}H_4O_{22}$, as $Gr_{24}H_4O_{22}$; these graphic compounds being regarded by Brodie as analogous to the oxides of silicon discovered by Wöhler and Buff (386_a).

the carbon which it held in combination is deposited, and by degrees a layer of very pure dense carbon is formed, possessed of a lustre resembling that of a metal. The density and appearance of this mass vary according to the temperature, and the gaseous pressure to which it has been subjected.

Pit coal is a substance originally of vegetable origin, which has become altered in appearance and composition by the combined action of heat and moisture under great pressure. The composition of coal varies considerably according to the extent to which these decomposing actions have advanced: the different varieties of coal will be noticed hereafter (951), but in all cases it consists, like vegetable matter in general, of carbon, hydrogen, and oxygen, with a small proportion of nitrogen; and in addition, it contains a variable quantity of saline and earthy substances, which always exist in the juices of plants, besides a variable amount of iron pyrites or bisulphide of iron. These saline matters are left, when the coal is burnt in an open fire-place, and constitute the ashes; whilst the carbon and hydrogen are entirely converted into carbonic acid and water, if an adequate supply of oxygen from the air be furnished; but the burning of coal, even in an open fire, is never complete, so that it gives off a quantity of gaseous and tarry matters, holding finely divided carbon or soot in suspension.* When the coal is heated in long closed iron cylinders, so constructed as to exclude atmospheric air, but to allow free escape for volatile matters, a large

* *Consumption of Smoke.*—When a quantity of fresh coal is thrown upon a hot fire, the coal immediately begins to undergo decomposition; various compounds of carbon with hydrogen being abundantly extricated in the form of gas or vapour: a portion of these immediately takes fire and burns with a bright, luminous flame, but a large proportion of these hydrocarbons, on coming into contact with the glowing embers, is further more or less completely decomposed, the carbon and hydrogen experiencing a separation from each other; the hydrogen, which is the most combustible element, becomes burned, or, if the supply of oxygen be inadequate, it passes off in the gaseous form, whilst the carbon, owing to the minute state of subdivision of its particles, is carried up the chimney suspended in the current of heated gases. By proper care, the volumes of black smoke ordinarily poured forth from the chimneys of our houses and factories, may, however, be prevented, and the annoyance due to this contamination of the atmosphere in our large towns to a great extent obviated; whilst a considerable saving of fuel may at the same time be effected.

The principles involved in the prevention of smoke are—1st, the supply of fuel in small quantity at a time, taking care to maintain a strong, steady fire, in order that the gases may be burned as fast as they are generated; and, 2nd, the supply of an adequate quantity of atmospheric air. The latter condition is not so easily accomplished in the furnaces of the manufacturer as might be supposed. The regulated supply of fuel in small quantities may obviously be ensured by due care on the part of the stoker, but it requires more labour and attention than is usually bestowed by him. Various contrivances have been from time to time proposed for effecting the prevention of smoke, one class of these having for their object the regular supply of fuel by mechanical

quantity of gaseous substances, containing the oxygen, hydrogen, and nitrogen, with a part of the carbon of the coal, passes off (1314), while the greater proportion of the carbon remains behind, and constitutes *coke*, which is the only one of the products that will be noticed at present. Coke is, chemically, the same substance

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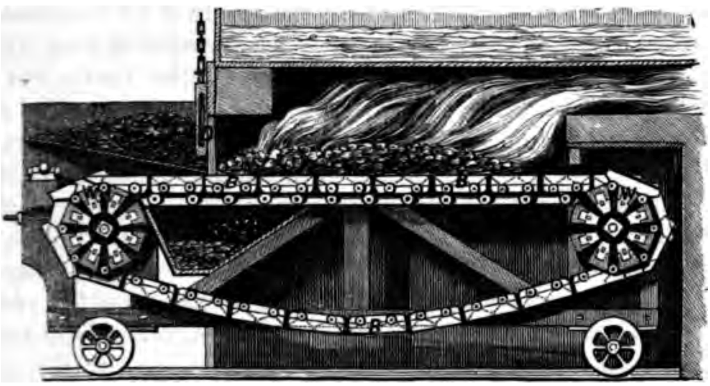
means, as is proposed by Juckes's apparatus, the essential points of which are shown in section in fig. 262.

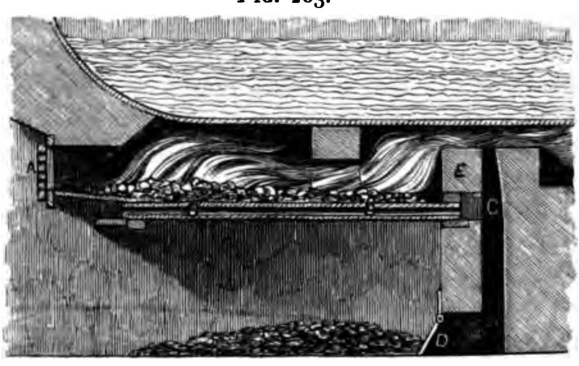
FIG. 262.



The fire-bars, B B, in this case consist of a series of endless chains, which are carried very slowly forward by machinery connected with the toothed wheels, W, W. A continuous but very gradual supply of fuel is furnished from the hopper, H, in front of the furnace, and the amount of coal thus admitted is regulated by raising or lowering the door D. This apparatus fulfils its object well, but the wear and tear of the fire-bars is considerable.

In another class of smoke-burning contrivances, the object is to burn the smoke which is formed in small quantity, by supplying air at a high temperature to the unburnt gases as they escape from the fire-place. Fig. 263 represents in section the plan adopted by Mr. F. C. Hills for attaining this object.

FIG. 263.



The coal is thrown into the fire by hand, but in moderate quantities at a time, the fire-door, A, being perforated for the admission of air. The fire-bars, B B, are tubular and allow the passage of air into the channel, C, which opens into the chimney just behind the bridge, E, of the fire-grate; the air becomes heated as it passes through the tubular bars, and, if the quantity thus admitted is not sufficient to complete the combustion of the unburned gaseous products as they escape, more air can be supplied from below by raising the damper, D.

as the graphite deposited from the gas, but in a less pure form, owing to the earthy matters which are mixed with it. As a fuel coke is often to be preferred to coal, since it burns without emitting any visible smoke; it has also the advantage of not swelling or caking together when heated, and thus the danger of choking the draught is avoided. The higher the temperature to which coke is exposed during its manufacture, the more dense does it become, and the better is it fitted for producing a steady and intense heat, when burned as fuel; though unless the supply of air be tolerably abundant, it burns less freely in this dense condition than when less compact. In order to furnish a coke suited for the use of locomotive engines, it is customary to construct coke ovens, which are usually built of brick, and lined with fire-bricks, the walls being from 2 to 3 feet in thickness, to economize heat: and this object is further effected by building several ovens together in one continuous piece of masonry. One of these ovens, 12 feet in internal diameter and 4 feet in height, will convert $3\frac{1}{2}$ tons of coal into coke in forty-eight hours. The oven has a sliding door in front, for the purpose of introducing and withdrawing the charge, and for regulating the admission of air, which plays over the surface of the heap and burns off the volatile matters, which escape by a short chimney. The combustion proceeds gradually, from above downwards: in about forty hours after commencing the operation, the door is completely closed, and the furnace left for 5 or 6 hours; at the end of that time the coke is withdrawn, and quenched with water. A bituminous coal, like the Newcastle coal, furnishes in this way a very dense lustrous coke, which splits into long columnar masses or prisms, as the temperature in the oven gradually falls when the door is closed. A fresh charge is introduced into the oven whilst its walls still remain red hot. The coke is never melted in this operation, and the appearances of fusion which it frequently exhibits are due to the liquefaction, by heat, of the bituminous portions of the coal, before they have undergone carbonization. A very pure form of carbon is frequently observed in the fissures of the mass, in the form of black fibres, closely resembling horsehair in appearance.

Coke may also be prepared, though with less advantage, by a smothered combustion of the coal in heaps, in a manner similar to that practised in making charcoal. Coke is subject to great variation in appearance and bulk, this variation depending on the kind of coal employed in producing it: it is, however, always more bulky than the coal that yields it.

(300) *Charcoal: Amorphous Carbon* (C_γ).—Carbon also exists

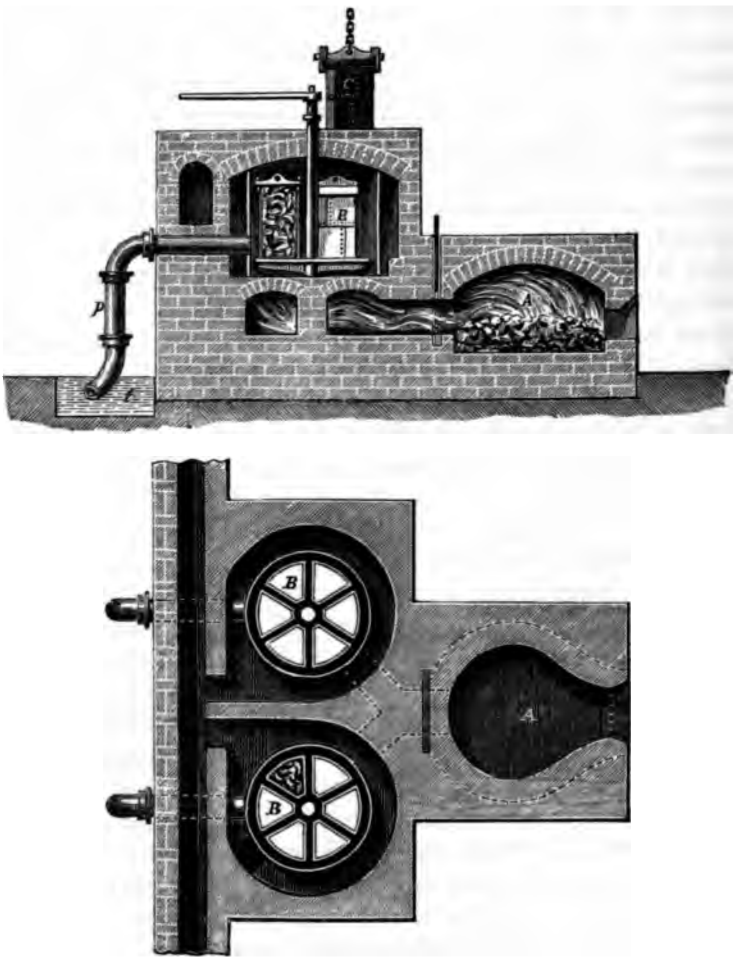
in a third form, distinct from that of graphite, and in this state it is amorphous, or entirely destitute of crystalline structure. *Lamp-black* is a variety of this kind of charcoal; it is largely manufactured by heating, in an iron pot, vegetable matters rich in carbon, such as resin or tar; the vapours thus disengaged are kindled, and burned in a current of air insufficient for their complete combustion; the hydrogen which these bodies contain, being the more inflammable ingredient, burns off first, leaving the carbon in the form of a very finely-divided powder, such as that which constitutes the visible portion of smoke. The smoky products of this imperfect combustion are made to pass through a large chamber, the walls of which are covered with coarse cloth, and here the lamp-black is deposited. Lampblack always retains a portion of some incompletely burned compounds of carbon and hydrogen. The purest form in which finely divided carbon can be obtained for chemical purposes is furnished by passing the vapour of oil of turpentine or of ether slowly through tubes maintained at a red heat; a fine powder of charcoal is deposited within them; but this, also, even if again heated intensely in closed vessels, always retains traces of hydrogen.

Tinder is another variety of carbon in the amorphous or uncrystalline form; but the most important variety is *Wood Charcoal*, which is largely manufactured by heating billets of wood to dull redness in cast-iron cylinders, set in the furnace either vertically or horizontally, and provided with a tightly fitting lid at one end. The best plan consists in enclosing the wood to be charred in a second lighter case, which can be easily introduced into and withdrawn from the fixed cylinder, which is set in masonry, and protected from the direct action of the flame by a casing of fire-brick. From this kind of iron retort proceeds a tube connected with a condensing apparatus, where the liquid products of the decomposition may be arrested, whilst the uncondensible gases pass on, and are directed into the fire-place, where they are consumed. After the heat has been continued for four or five hours, the end of the outer cylinder is removed, the inner case with its charge is withdrawn, and the whole, whilst still red hot, plunged into an extinguisher or iron case, provided with a tightly fitting lid, which protects it from the action of the air; in this condition it is left to cool gradually.

A convenient arrangement for this purpose is shown in fig. 264, which exhibits in section and in plan the method adopted by Mr. F. C. Hills for economizing the waste heat from the coke oven represented at A. Each of the carbonizing chambers, B, B, contains six sheet-iron cases, which can be separately raised or

lowered by machinery as shown at c. The volatile products pass off by the pipe *p*, and are transmitted through a coil of pipes contained in the condensing tank *t*.

FIG. 264.



In countries where wood is abundant, the charcoal is manufactured by a much ruder method. A plot of ground is levelled in or near the forest, a stake is driven into the ground, and a quantity of brushwood placed around its base, and logs of wood are piled up regularly round the stake so as to form a mound, which is partially covered up with powdered charcoal, leaves, turf, and earth; the heap is then fired by introducing lighted fagots into an aperture left at the base of the mound for this purpose; large quantities of moisture are presently exhaled, and when the whole mass is

thoroughly ignited, it is still more closely covered up from the air, the workmen regulating the admission of air as circumstances require; it is then allowed to burn out. When quite cold, the earth employed to stifle the combustion is removed, and the charcoal is fit for use. The combustion of one part of the wood is thus employed as a source of heat for charring the rest. Charcoal prepared in this manner is, for the purposes of fuel, preferable to that made in cylinders; it is denser and is more completely deprived of volatile matters, because the heat to which it is exposed is much more intense, and is continued for a much longer period. If the diameter of the heap be 30 feet or more, the operation is not complete in less than a month. A slow combustion is found to yield more charcoal than one which is rapidly effected. The resulting charcoal retains the form of the wood, but it is much reduced in size, generally not amounting to more than three-fourths of the bulk of the wood, and never exceeding one-fourth of its weight.

Experience shows it to be much more economical to employ dry wood in the preparation of charcoal than wood in its green condition. Karsten found that 100 parts of recently felled wood, dried at 212°, lost 57 parts; by raising the temperature to 302° the loss upon the original weight amounted to not less than 67 parts; and the 33 parts of dry residue when charred left 25 parts of charcoal; but 100 parts of the same wood, if charred without any preliminary drying, left only 14 parts of charcoal. This remarkable difference in produce depends upon the decomposing action of charcoal at a high temperature upon water, in consequence of which much of the carbon escapes in the gaseous state in the form of carbonic oxide, whilst the hydrogen of the water also passes off as gas.

The object of preparing charcoal as a fuel is to get rid of moisture and volatile matters, which, at the moment of their formation, greatly reduce the temperature of the burning mass, owing to the large quantity of heat which they carry off in the latent state. Charcoal also contains in the same bulk a larger amount of carbon than the wood which furnished it, and by supplying a more compact fuel concentrates into a smaller space the heat which it emits, a condition which, in metallurgical operations demanding a high temperature, is often of the greatest importance.

In the economy of material to be used as a combustible, it is not sufficient to consider simply the absolute amount of heat which a given weight of the fuel emits whilst burning. The radiating power of a solid mass of fuel is much higher than that of a gaseous combustible, but the temperature of flame is very high. A fuel which burns with flame is therefore necessary where it is

needful to communicate an elevated temperature to objects at a distance from the fire-grate, or to raise large masses to a uniform temperature. Wood and bituminous coals are, consequently, particularly useful in the glass furnace and in the porcelain kiln, whilst in heating boilers, and objects in which direct radiation can act with its full effect, coke, anthracite, and coal which burns with but little flame, are especially valuable. In an ordinary open fire, these flameless fuels are also the most useful, as the heat is thrown off by them into the room most completely, instead of being carried up the chimney with the gaseous products.

Charcoal never consists solely of pure carbon. According to the experiments of Violette, 100 parts of black alder (*Bourdaine*) wood, charred at the following temperatures, gave amounts of charcoal progressively diminishing; but the per-centage of carbon in the residual charcoal was found to increase, as shown in the table:—

Temperature of charring. F°.	Per-centage of charcoal.	Per-centage of carbon in charcoal.
480°	50	65
570°	33	73
750°	20	80
2730°	15	96

A peculiar kind of charcoal, but imperfectly burned, and of a reddish-brown colour, termed by the French *charbon roux*, is occasionally prepared for the manufacture of the gunpowder used for sporting purposes. Powder made with this charcoal absorbs moisture more rapidly than ordinary gunpowder. *Charbon roux* is procured by forcing steam, under a pressure of about two atmospheres, through a coil of heated pipe, and directing this superheated steam, at about 540°, into the iron cylinder containing the wood; in a few hours the charring of the wood is effected. The following is stated by Regnault to be its average composition in 100 parts:—

Carbon	71·42
Hydrogen . . .	4·85
Oxygen and Nitrogen . .	22·91
Ash	0·82

Animal Charcoal, or ivory black, is prepared by heating bones in cylinders in a manner similar to that employed for wood charcoal.

(301) ***General Properties of Carbon.***—Carbon in all the forms above mentioned is chemically the same. At atmospheric temperatures it is one of those substances in which chemical affinity

exhibits least activity; consequently a superficial charring is frequently resorted to to protect wood from decay, as in the case of piles which are driven into mud or into the beds of rivers, to serve as foundations. For the same reason it is a common practice to char the interior of tubs and casks destined to hold liquids. Lampblack furnishes the most indestructible of black pigments, and has long been employed on this account as the basis of printing ink. The diamond is a non-conductor of electricity; in its other forms carbon is an excellent conductor, ranking next to the metals in this respect. In a state of fine subdivision it is a bad conductor of heat, but its conducting power increases with its density. Finely divided charcoal is usually stated to have strong antiseptic powers. It certainly has a remarkable action upon putrescible substances; but Stenhouse has shown that this action consists in a rapid process of oxidation dependent upon the power which charcoal, when in a finely divided state, possesses of condensing oxygen. Animal matter in an advanced state of putrefaction loses all offensive effluvia when covered with a layer of charcoal; it continues to decay, but without emitting any odour, till at length all the carbon is dissipated as carbonic acid, the hydrogen as water, and the nitrogen remains as nitric acid. The remarkable power possessed by charcoal of absorbing various bodies, particularly colouring matters and many bitter principles, when in a finely divided state (53), as well as its property of condensing a large proportion of gaseous matters within its pores (62), has been already mentioned. So rapid is this action, that Stenhouse has proposed to use a respirator filled with charcoal, to protect the mouth and nostrils in an infected atmosphere; and the employment of trays of powdered wood charcoal in dissecting-rooms, in the wards of hospitals, and in situations where putrescent animal matter is present, is found to exert a most beneficial influence in sweetening the atmosphere by absorbing and decomposing the offensive gases. These properties render charcoal a valuable material in the construction of filters, not only for decolorizing purposes, but also for assisting in purifying water for domestic use.

Carbon is usually regarded as infusible and not volatile; but in the course of some experiments with a voltaic battery of intense energy, consisting of 600 cells of Bunsen's construction, connected so as to form a battery of 100 pairs of 6 cells each, Despretz found on operating upon carbon points in an exhausted receiver, that the vessel became filled with a dark cloud, which was deposited upon the sides of the glass as a black crystalline powder; and by exposing charcoal obtained from pure sugar, or from essence of tur-

pentine, to the action of the battery in a small crucible of pure charcoal connected with the positive electrode, the whole of the charcoal powder became cemented into a coherent mass which appeared to have been fused, and which exhibited the properties of graphite.

At high temperatures carbon combines rapidly with oxygen, and will remove it from a great number of its compounds, especially from the oxides of the metals; hence the various forms of carbon are very extensively employed in the reduction of these substances to the metallic condition. The deoxidizing power of carbon is sometimes exerted at the ordinary temperature of the air. Schönbein found that the salts of the sesquioxide of iron may be reduced to the condition of protosalts, by simply agitating their solutions with charcoal powder, and the salts of the red oxide of mercury are converted into those of the suboxide.

Sulphur is the only non-metallic element besides oxygen with which carbon can be made to unite directly, and a high temperature is required in this case also to effect the combination (586). Charcoal decomposes steam at a red heat; hydrogen is liberated, and a mixture of carbonic oxide and carbonic acid is formed.

The compounds of carbon with the metals are termed *carburets* or *carbides*.

(302) *Synthesis of Carbonic Acid.*—Since a knowledge of the composition of carbonic acid is a fundamental datum for the analysis of organic compounds, the proportion in which oxygen combines with carbon to produce carbonic acid has been determined with the greatest care, by the combustion of weighed quantities of diamond, of graphite, and of charcoal, in a stream of dry oxygen. The apparatus employed for this purpose is indicated in fig. 265. A represents a gas-holder filled with oxygen; B a

FIG. 265.

tube containing fragments of caustic potash, or pumice-stone moistened with sulphuric acid, for removing all traces of moisture

from the oxygen; *c d* is a tube of hard glass traversing the sheet-iron furnace, E. At *c* is a platinum tray containing the weighed portion of diamond or graphite; the front of the tube *d* is occupied by a column of oxide of copper. The apparatus is filled with dry oxygen by opening the stopcock of the gas-holder, A, to a regulated distance, and the fore-part of the tube, *d*, is brought to a red heat by means of lighted charcoal; the heat is then applied to the spot, *c*, where the carbon lies. The carbon burns and becomes converted into carbonic acid, which passes on through the column of heated oxide of copper; F is a weighed tube, filled with chloride of calcium, which, if water were present, would be found to increase in weight, but in which no deposit of moisture is formed if the experiment be properly conducted. The carbonic acid passes on, and is absorbed by a strong solution of potash which is contained in the bulbs of the Liebig's apparatus, shown at G. The excess of oxygen absorbs moisture as it passes through this liquid, but before it is allowed to escape into the air it is rendered perfectly dry by causing it to pass through an additional tube, H, filled with fragments of caustic potash. The increase in weight acquired by the tubes G and H furnishes the weight of the carbonic acid corresponding to the quantity of carbon consumed, and the quantity of carbon burned is ascertained by weighing the platinum tray and its contents after the experiment has terminated. By experiments conducted upon this principle it has been determined that 6 parts of carbon require for conversion into carbonic acid exactly 16 parts of oxygen (Dumas and Stas, *Ann. de Chimie*, III. i. 5).

Diamond, graphite, and charcoal, are thus shown to be chemically the same substance, though they differ entirely in properties; these three conditions being allotropic modifications of carbon (84), the differences in properties arising not from differences in their chemical nature, but in their molecular arrangement.

If a piece of pure carbon be burned in a jar of oxygen over mercury, it will be found after the combustion is over, and the gas has cooled to the initial temperature of the oxygen, that its volume has undergone no permanent change: the bulk of the oxygen, therefore, is not altered by this combination; the carbonic acid which is formed occupies precisely the same space as the oxygen which produced it.

(303) CARBONIC OXIDE: *Sp. Gr.*, 0·967; *Comb. Vol.*, 2.*—It has been stated that carbonic acid is wholly deprived of its oxygen

* Probably it should be $(CO)_2=28$ with a combining volume of 4. Gerhardt's corresponding formula with the double atomic weights of carbon and oxygen would be $CO=28$.

when heated with potassium; but if some metal, such as zinc or iron, which has a less powerful affinity for oxygen, be substituted for the potassium, the carbonic acid will only be partially deoxidized; the metal will deprive it of exactly half the oxygen which it contains, and a new gaseous body, termed *carbonic oxide*, will be produced. The bulk of this new gas is exactly equal to that of the carbonic acid that furnished it.

Preparation.—1. Carbonic oxide may be conveniently prepared by mixing powdered chalk with an equal weight of iron or zinc filings, and exposing the mixture to a red heat in a gun-barrel. The chalk when ignited gives off carbonic acid, which in contact with the heated metal is decomposed; oxide of iron or of zinc is formed, quick-lime remains in the retort mixed with the metallic oxide, and the carbonic oxide gas may be collected over water, in which it is but slightly soluble. These chemical changes may be represented in the following manner:—

Decomposition of Carbonic Acid by Zinc.

Before decomposition.		After decomposition.
50 = 1 eq. of chalk	28 = 1 eq. lime (CaO)	remains.
	14 = 1 eq. carbonic oxide (CO)	set free.
	8 = 1 eq. oxygen, O	
32·7 = 1 eq. zinc (Zn)		40·7 { 1 eq. oxide of zinc (ZnO);

or in symbols:—

$$CaO, CO_2 + Zn = CaO + ZnO + CO.$$

2.—Carbonic oxide is often produced abundantly in the ordinary process of combustion in stoves and furnaces: this mode of its formation is important, for it exercises a material influence upon the economy of combustion, inasmuch as all the carbonic oxide thus carried off unburnt represents so much fuel wasted; while in many metallurgic operations the carbonic oxide so produced plays a conspicuous part in the reduction of the ore to the metallic state. It is owing to the production of carbonic oxide that anthracite can be employed in roasting the copper ores at Swansea, flame being essential to the due performance of the process (732). The formation of carbonic oxide in an open fire which is burning steadily without emitting smoke is often evidenced by the flickering blue flame seen playing over the glowing embers. In this case carbonic acid is first formed at the bottom of the grate, from the free access of air to this part of the burning fuel; the carbonic acid gas as it traverses the red-hot coke enters into combination with an additional quantity of carbon. The acid, by losing half

its oxygen, is converted into its own bulk of carbonic oxide, and at the same time the carbon of the heated fuel which has entered into combination with this removed oxygen furnishes another equal quantity of the same gas: and the heated carbonic oxide takes fire as soon as it mixes with the air which passes over the upper surface of the fire. The reaction between the hot carbon and carbonic acid may be thus represented: $CO_2 + C = 2\,CO$.

3.—Carbonic oxide may also be formed in several other ways. Half an ounce of the yellow prussiate of potash, if finely powdered, placed in a retort, and heated with 4 or 5 ounces of oil of vitriol, yields more than a gallon of the pure gas (Fownes). Care is requisite in applying the heat, because when the temperature rises to a certain point the extrication of the gas takes place with tumultuous rapidity. The reaction is in this case of a complicated nature, but is expressed by the annexed symbols:—

$$\overbrace{K_2Fe\,C_6N_3}^{\text{Ferrocyan. potass.}} + \overbrace{6\,HO}^{\text{Water.}} + \overbrace{6\,(HO,\,SO_3)}^{\text{Sulphuric acid.}}$$

give

$$\overbrace{6\,CO}^{\text{Carb. oxide.}} + \overbrace{2\,(KO,\,SO_3)}^{\text{Sulphate potash.}} + \overbrace{FeO,\,SO_3}^{\text{Sulphate iron.}} + \overbrace{3\,(H_4NO,\,SO_3)}^{\text{Sulphate ammonia.}}$$

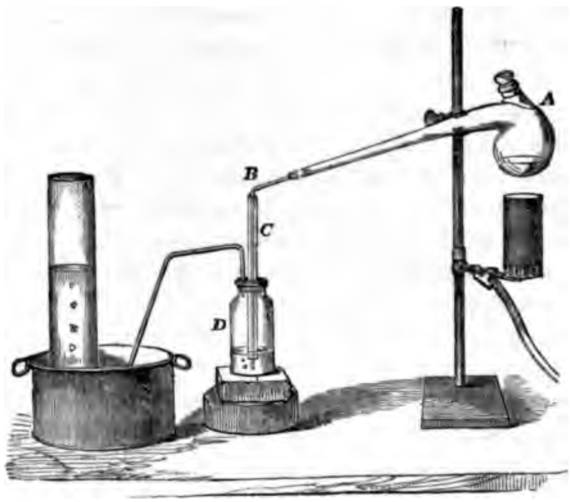
One atom of ferrocyanide of potassium and 9 atoms of water produce 6 of carbonic oxide, 2 of potash, 1 atom of protoxide of iron, and 3 atoms of oxide of ammonium; and these bases all combine with sulphuric acid to form sulphates, some of which afterwards form double salts with each other.

4.—Another method by which carbonic oxide may be obtained with facility consists in heating oxalic acid with 5 or 6 times its weight of oil of vitriol. The oxalic acid is thus deprived of water, and is resolved into a gaseous mixture consisting of equal measures of carbonic acid and carbonic oxide: by allowing the mixed gases to pass through a vessel filled with a solution of potash, or with milk of lime, the carbonic acid is absorbed, and the carbonic oxide may be collected in a state of purity. The decomposition may be thus explained:—

$$\overbrace{2\,HO,\,C_4O_6}^{\text{Oxalic acid.}} = \overbrace{2\,HO}^{\text{Water.}} + \overbrace{2\,CO}^{\text{Carb. oxide.}} + \overbrace{2\,CO_2}^{\text{Carb. acid.}}.$$

A convenient mode of washing the gas is shown at B, fig. 266; the bent tube is connected to the neck of the retort, A, and passes to the bottom of a wider tube, C, open both at top and bottom, which passes into the washing bottle, D: a moveable gas-tight joint, which can be mounted or dismounted in a moment, is thus obtained.

FIG. 266.



Properties.—Carbonic oxide is a transparent colourless gas, with a faint oppressive odour. It is much lighter than carbonic acid, having a specific gravity of 0·967 (Wrede.) All attempts at its liquefaction have as yet been unsuccessful. It is but very sparingly soluble in water, 100 parts of this liquid dissolving 3·28 parts at 32° and 2·43 at 59° (Bunsen). When respired, even though diluted with air, it acts as a direct poison, producing a peculiar sensation of oppression and tightness of the head. It does not support combustion, but burns itself with a beautiful, pale blue light, producing by its combination with oxygen carbonic acid only. A solution of dichloride of copper in hydrochloric acid, or of a salt of dioxide of copper in ammonia, gradually absorbs carbonic oxide if agitated with it. The compound with dichloride of copper crystallizes as $CO, Cu_2Cl + 2\ Aq$. Carbonic oxide is absorbed by potassium if the metal be heated to about 176° in the gas, and according to Brodie, the combination occurs in the proportion of $2\ CO + K$. This property is sometimes employed for separating carbonic oxide from its mixture with other inflammable gases in the process of analysing mixtures of such gases.

Carbonic oxide has been supposed to form the radicle of a numerous series of compounds; it even enters directly into combination with hydrate of potash when heated with it, converting it into formiate; $KO, HO + 2\ CO = KO, C_2HO_3$ (1173).

Composition.—The chemical composition of carbonic oxide may be ascertained in the following manner:—Introduce into the bent eudiometer (fig. 257) a certain measure, say 20 parts of

carbonic oxide, then add 20 measures of pure oxygen; pass the electric spark with the precautions already described: the 40 measures of gas will become diminished to 30 measures. If a little solution of potash be introduced, 20 measures of the residual gas will disappear, leaving 10 measures of unaltered oxygen: the 20 measures of gas absorbed are carbonic acid. Now carbonic acid contains its own bulk of oxygen, but the 20 measures of carbonic oxide have required only 10 measures, or half their bulk of oxygen to convert them into carbonic acid. Carbonic oxide therefore must have contained the other 10 measures of oxygen; in other words, half its bulk of oxygen. But the specific gravity of carbonic oxide is 0·9674; deduct from this

0·5528 = half the density of oxygen

0·4146; this remainder is the weight of the carbon combined with 0·5528 of oxygen.

Now 0·5528 : 0·4146 : : 8 : 6. The proportion by weight of oxygen to carbon in carbonic oxide is therefore as 8 to 6, or 1 atom of each, and its composition may be thus represented:—

		By weight.		By volume.			Sp. Gr.
Carbon,	C =	6	or 42·86	2 ?	or 1 ?	=	0·4146
Oxygen,	O =	8	57·14	1	0·5	=	0·5528
Carb. oxide,	CO =	14	100·00	2	1·0		0·9674

Carbonic oxide and carbonic acid, widely as they differ in properties, consist, it is evident, of the same elements; but the proportion of the two elements is different in the two cases. Carbonic oxide is the compound of carbon that contains the smallest proportion of oxygen, the relative composition of the two bodies being:—

				C.		O.		Carbon.		Oxygen.
Carbonic oxide	CO	= 14	or	6	+	8	=	42·86	+	57·14
Carbonic acid	CO_2	= 22		6	+	16	=	27·28	+	72·72
								In 100 parts.		

CHAPTER V.

COMPOUNDS OF NITROGEN WITH OXYGEN AND WITH HYDROGEN.

§ I. Compounds of Nitrogen with Oxygen.

(303 *a.*) The affinity of nitrogen for oxygen is much feebler than that of either carbon or hydrogen or oxygen, so that it is not easy to procure their direct union,—especially as the temperature emitted

by nitrogen and oxygen in the act of combination is comparatively low. Nitrogen, notwithstanding, forms with oxygen five distinct compounds, containing, respectively, 1, 2, 3, 4, and 5 atoms of oxygen with 1 atom of nitrogen.

These compounds have been named

			By weight.		In 100 parts.	
			N.	O.	Nitrogen.	Oxygen.
Protoxide of Nitrogen,	NO, = 22	or	14 +	8	63·64 +	36·36
Deutoxide of Nitrogen,	NO_2, = 30		14 +	16	46·67 +	53·33
Nitrous acid,	NO_3, = 38		14 +	24	36·85 +	63·15
Peroxide of Nitrogen	NO_4, = 46		14 +	32	30·44 +	69 56
Nitric acid	NO_5, = 54		14 +	40	25·93 +	74·07

(304) NITRIC ACID ($NO_5=54$); HYDRATED NITRIC ACID ($HO, NO_5=63$).—The most important of the compounds of oxygen with nitrogen is nitric acid, which when in combination with water was formerly called aquafortis. It was known to the alchemists, but its true composition was first determined by Cavendish in 1785. When nitrogen is mixed with 12 or 14 times its bulk of hydrogen, and a jet of the mixed gas is allowed to burn in air or in oxygen, the water which is formed has a sour taste and an acid reaction, owing to the simultaneous formation of a small quantity of nitric acid. In this case the nitrogen burns by the aid of the heat developed during the combustion of the hydrogen, and the nitric acid combines at once with the water formed, which much increases its chemical stability. It was, indeed, owing to the accidental production of nitric acid in the course of his experiments on the formation of water by the combustion of hydrogen, that Cavendish was induced to institute the train of researches which terminated in this important discovery.

If 2 volumes of nitrogen be mixed with 5 volumes of oxygen, and introduced into the bent eudiometer (fig. 257) and the tube be filled up with an infusion of blue litmus in distilled water, a series of electric sparks may be transmitted through the mixture by means of a Ruhmkorff's coil; under these circumstances the two gases will slowly combine, and the litmus will be reddened. The heat of the spark determines the combination of the gases just at the spot through which it passes, but the action does not extend further. In like manner, if a number of sparks be passed from the electrical machine, between two metallic points, over moistened litmus paper, in air, a red spot will be produced upon the paper, owing to the formation of nitric acid in minute quantity by the combination of oxygen with nitrogen. During stormy weather, and indeed whenever a flash of lightning passes through a

moist atmosphere, the same compound is produced in appreciable quantity. Indeed, it is rare to meet with rain water in which traces of nitrate of ammonia may not be detected, if the experiment is made with accuracy. Ammonia likewise yields nitric acid under certain circumstances by slow oxidation (311).

Nitric acid also occurs in combination with potash or soda, in the form of an efflorescence on the soil, especially in tropical climates, as in some parts of India and Peru. The compound formed with potash constitutes the nitre or saltpetre of commerce. The nitrates of the alkalies are also often present in the water of wells in towns or in the vicinity of cemeteries, the nitric acid being in these cases produced by the oxidation of azotised animal matters, as they undergo decomposition during the percolation of their aqueous solution through the soil.

Preparation.—It is from one of the nitrates that the acid is always obtained for chemical purposes. When nitrate of potash is heated with a powerful acid, such as the sulphuric, it is decomposed; a combination of sulphuric acid with potash remains in the retort, whilst the more volatile nitric acid distils over, and may be condensed in the usual manner. The method of procuring nitric acid offers a good example of the general principle upon which acids which admit of being distilled without experiencing decomposition are obtained from their salts. In preparing nitric acid on the small scale, equal weights of nitre and oil of vitriol are placed in a glass retort, and the distillation is proceeded with in the manner shown in fig. 119, Part I., p. 260. The result of the reaction may be traced as follows:—

Preparation of Nitric Acid.

Before decomposition.		After decomposition.
101 = 1 eq. Nitrate of Potash	54 = 1 eq. Nitric acid	63 { 1 eq. Liquid nitric acid.
	47 = 1 eq. Potash	
98 = 2 eq. Oil of vitriol	9 = 1 eq. Water	
	40 = 1 eq. Sulphuric acid	136 { 1 eq. Acid sulphate of potash.
	49 = 1 eq. Oil of vitriol	

or—

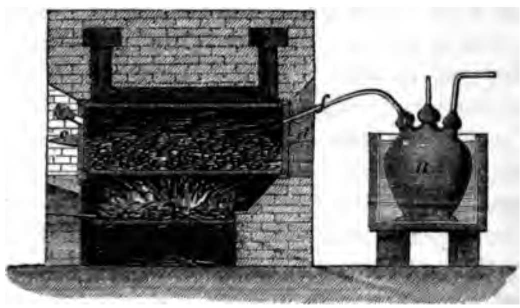
$$KO, NO_5 + 2\ (HO, SO_3) \text{ give } HO, NO_5 + (KO, HO, 2\ SO_3).$$

During the distillation red fumes appear in the retort, arising from a partial decomposition of the acid, and a formation of some of the lower oxides of nitrogen, whilst a yellowish corrosive liquid is condensed in the receiver: this liquid is concentrated nitric acid

(HO, NO_5); it fumes strongly in the air, and emits a powerful, irritating odour.

On the large scale, iron retorts, fig. 267, coated with fire-clay on the inside of the upper part, where they are exposed to the acid vapours, are employed for the distillation, and nitrate of soda is substituted for nitrate of potash, as it is a cheaper salt, and likewise contains 9 per cent. more nitric acid than nitrate of potash. The cylinders or retorts are arranged in pairs in a furnace, so that each fire heats two cylinders, as shown in the section 1 :—

1. Fig. 267. 2.



The cylinders are supplied with a moveable lid, *c*, *d*, at each end. The nitrate is introduced into the retort, A, through the opening at *c*, which is closed during the distillation by a stone lid, fitted accurately to the aperture; and the oil of vitriol is added by a funnel at *e*, after the retort is closed. As soon as the acid is introduced, the funnel is withdrawn, and the opening at *e* is closed with a plug. The nitric acid as it distils over passes through the pipe *f*, and is condensed in a series of stoneware bottles, the first of which is seen at B. The acid which is collected in the first receiver is always contaminated with sulphuric acid, and that in the last is rather dilute, as water is placed in it to condense the nitrous fumes.

Upon the large scale it is customary to employ a proportion of sulphuric acid smaller than that used when the distillation is performed in glass vessels, as it is quite possible to effect a complete decomposition of the nitrate by heating it with one-half its weight of oil of vitriol. Under these circumstances, however, a higher temperature is needed to expel the last portions of acid, and a considerable quantity of the nitric acid is thereby decomposed and wasted. The residue in the retort, when the smaller quantity of sulphuric acid is used, is much less soluble in water, and consequently is much more difficult of removal: but in the iron cylinder of the manufacturer this is of no moment, because the saline

mass can easily be detached by the use of iron tools when the distillation is at an end.

The cause of these differences lies in the fact, that sulphuric acid forms with potash two different compounds, one of which contains twice as much acid as the other. When nitre and sulphuric acid are mixed in the proportion of 2 equivalents of each, half the nitre only is decomposed so long as a gentle heat only is employed, and the acid sulphate of potash is formed. The nitric acid thus liberated distils over readily. The following diagram shows the form of this reaction :—

Before decomposition.			After decomposition.
202=2 eq. of nitre 2 (KO,NO_5)	101=1 eq. Nitre,	(KO,NO_5)	101=1 eq. Nitre
	54=1 eq. Nitric acid	(NO_5)	63 1 eq. liquid nitric acid, (HO,NO_5)
	47=1 eq. Potash	(KO)	
98=2 eq. of oil of vitriol, 2 (HO,SO_3)	9=1 eq. Water	(HO)	
	40=1 eq. Sulph. acid	(SO_3)	136 1 eq. of Acid sulphate of potash, ($KO, HO, 2\ SO_3$)
	49=1 eq. Oil of vit.	(HO,SO_3)	

The same change may also be thus represented in symbols :—

$$2\,(KO,NO_5)+2\,(HO,SO_3)=(KO,NO_5)+(HO,NO_5)+(KO,HO,\ 2\ SO_3).$$

As soon as the first half of the nitric acid has passed over, the temperature begins to rise, and the acid sulphate of potash then reacts on the undecomposed nitre; the second half of the nitric acid is liberated, but at the same time is partially decomposed toward the end of the operation, and the whole of the potash remains in combination with sulphuric acid in the form of the sparingly soluble neutral (or normal) sulphate. This second stage of the decomposition is exhibited in the subjoined equation, which will be easily understood from the foregoing explanation :—

$$(KO,NO_5)+(KO,HO,\ 2\ SO_3)=HO,\ NO_5+2\,(KO,SO_3).$$

When, on the other hand, 2 equivalents of sulphuric acid are used to 1 equivalent of nitre, the whole of the potash is at once converted into the acid sulphate, so that the whole of the nitric acid is liberated immediately, and distils readily :—

$$(KO,\ NO_5)+2\,(HO,SO_3)\text{ give }(HO,\ NO_5)+(KO,HO,\ 2\ SO_3).$$

Properties.—Nitric acid, in the most concentrated form in which it can by this process be obtained, is, when pure, a colourless, limpid, fuming, powerfully corrosive acid liquid, of sp. gr. 1·520. It is the highest known oxide of nitrogen, and for each atom of nitrogen contains 5 atoms of oxygen, combined with

1 atom of water: 100 parts of this liquid contain 85·72 of the anhydrous nitric acid. It is very readily decomposed, as mere distillation always produces its partial decomposition. Exposure to the light of the sun has a similar effect. At 184° it begins to boil, and freezes at about —40°. Nitric acid parts very readily with a portion of its oxygen to the metals, and to combustible bodies. If it be dropped into hot finely powdered charcoal, the charcoal burns vividly; if mixed with a little oil of vitriol and poured into oil of turpentine, the mixture bursts into flame. Sulphur, phosphorus, and iodine are also oxidized by it—the phosphorus with great violence. Nitric acid is one of the most corrosive substances known. It rapidly destroys all animal textures, and, if somewhat diluted, stains the skin, wool, feathers, and all albuminous bodies, of a bright yellow colour. Nitric acid acts violently upon tin or iron filings, especially if they be previously moistened with a few drops of water, and indeed it attacks most of the metals, except gold, platinum, rhodium, and iridium; hence it is constantly employed by the chemist as an oxidizing agent.

The action of nitric acid upon the metals is instructive, and it may serve to illustrate the manner in which metallic bodies are attacked by the acids generally:—The metals will enter into direct combination with many of the simple non-metallic bodies: thus antimony will unite directly with chlorine, and will even take fire if allowed to fall into this gas in fine powder. Iron will burn in oxygen: and copper turnings, if mixed with powdered sulphur, will combine with the sulphur on the application of heat, emitting a vivid glow of light. But no metal will unite directly with an acid; in order that combination between them should occur, it is necessary that the metal should be in the form of oxide. This oxidation may, however, be effected at the same time that the acid is presented to the metal, and the formation of the oxide and its solution in the acid may appear to occur simultaneously. Zinc, for example, does not unite as zinc with sulphuric acid: when this metal is placed in diluted sulphuric acid, the oxygen is supplied from the water which is decomposed, oxide of zinc is produced, and is immediately dissolved by the acid, whilst the hydrogen escapes in the gaseous form. When a metal such as copper or silver is dissolved by nitric acid, a preliminary oxidation is equally necessary; but owing to the facility with which nitric acid is deprived of a part of its oxygen, this oxidation is usually effected at the expense of the nitric acid, which is decomposed more readily than water is; some of the lower oxides of nitrogen are liberated in the form of ruddy fumes, whilst the compound of the metal with oxygen becomes dis-

solved in another portion of the acid which has not undergone decomposition. The exact nature of the decomposition which the nitric acid experiences varies in different cases. Silver, when allowed to become dissolved slowly in the cold, in an excess of diluted nitric acid, produces nitrous acid (NO_3) which remains in solution: thus $2\,Ag + 3\,NO_5$ becomes $2\,(AgO, NO_5) + NO_3$, and the metal is dissolved without evolution of gas; a similar effect is also produced by palladium. With metals which, like copper and mercury, have a somewhat stronger affinity for oxygen, deutoxide of nitrogen (NO_2) is disengaged in large quantity; for example, $3\,Cu+4\,NO_5$ yields $NO_2+3\,(CuO, NO_5)$: and if the metal have a still more powerful tendency to combine with oxygen, as is the case with zinc, the protoxide of nitrogen (NO) is, if the acid be dilute, amongst the gases disengaged: $4\,Zn + 5\,NO_5$ would produce $NO+4\,(ZnO, NO_5)$. Zinc and tin also decompose water as well as nitric acid when dissolved in the acid, setting hydrogen free, whilst the hydrogen at the moment of its liberation completely deprives a portion of nitric acid of its oxygen, and forms ammonia (H_3N), by entering into combination with the liberated nitrogen; for instance, $8\,Zn+8\,(HO, NO_5) = 8\,(ZnO, NO_5) + 8\,H$, and $HO, NO_5 + 8\,H$ yield $6\,HO+H_3N$. In order to produce a rapid oxidation of the metals it is best to dilute the acid until its specific gravity is between 1·25 and 1·35; the action is then very brisk. The monohydrated acid, in fact, is without action upon iron, bismuth, and many other metals, at ordinary temperatures. The presence of nitrous acid in nitric acid greatly increases its oxidizing power, for owing to the instability of nitrous acid it parts with its oxygen very readily.

When concentrated nitric acid is exposed to the air, it absorbs moisture; and if mixed with water it emits a sensible amount of heat, owing to the formation of another hydrate of much greater stability. This stable hydrate ($HO, NO_5+3\,Aq$) contains 4 atoms of water for every atom of the anhydrous body NO_5: it has a specific gravity of 1·424, and is composed of 60 per cent. of anhydrous NO_5, and 40 of water. It has a higher boiling point than the protohydrate, and distils at 250° without change. A weaker acid, when heated, parts with its water, till it arrives at this density, and a stronger acid, in like manner, loses acid; the liquid in the retort being eventually, in both cases, reduced to the hydrate with 4 Aq. of sp. gr. 1·424. According to Bineau, the vapour of this hydrate has a density of 1·243. Ten volumes of this vapour contain 1 equivalent of the acid.

The following table indicates the per-centage of the anhydrous

compound (NO_5) contained in aqueous solutions of nitric acid of various specific gravities :—

Strength of Nitric Acid (Ure).

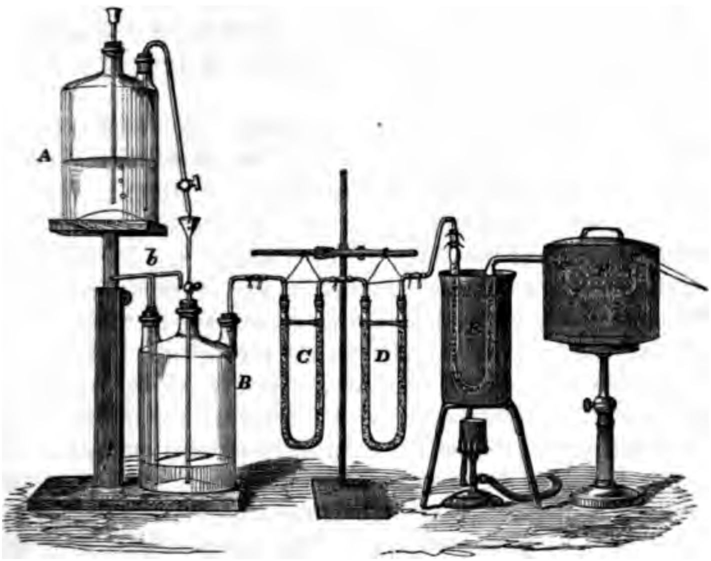
Specific gravity.	NO_5 in 100 parts by weight.	Specific gravity.	NO_5 in 100 parts by weight.
1·5000	79·700	1·2887	39·053
1·4940	77·303	1·2705	36·662
1·4850	74·918	1·2523	34·271
1·4760	72·527	1·2341	31·880
1·4670	70·136	1·2148	29·489
1·4570	67·745	1·1958	27·098
1·4460	65·354	1·1770	24·707
1·4346	62·963	1·1587	22·316
1·4228	60·572	1·1403	19·925
1·4107	58·181	1·1227	17·534
1·3978	55·790	1·1051	15·143
1·3833	53·399	1·0878	12·752
1·3681	51·068	1·0708	10·361
1·3529	48·617	1·0540	7·970
1·3376	46·226	1·0375	5·579
1·3216	43·835	1·0212	3·188
1·3056	41·444	1·0053	0·797

(304 *a*) *Nitric Anhydride*, or *Anhydrous Nitric Acid* $(NO_5)_2$.—This substance is a very unstable compound, which may be obtained in the form of perfectly transparent, brilliant, colourless crystals, derived from the right rhombic prism: they melt at 85° F., and boil at 113°: at about this temperature the compound begins to undergo decomposition. Sometimes the crystals, even if kept in sealed tubes, undergo decomposition at the ordinary atmospheric temperature, and the tube bursts with a dangerous explosion from the pressure exerted by the liberated gases. The crystals are dissolved rapidly by water, emitting much heat, and producing ordinary hydrated nitric acid.

In order to procure the anhydride, a uniform current of perfectly dry chlorine gas is transmitted very slowly over crystals of well-dried nitrate of silver: the salt is at first heated to about 200° till the decomposition has commenced, and the temperature is then lowered to about 150°. The operation is one of considerable delicacy, and requires attention to a number of minute precautions, for the details of which the reader is referred to Deville's paper (*Ann. de Chimie*, III. xxviii. 241). The apparatus required is shown in fig. 268. A is a vessel of concentrated sulphuric acid: the acid is drawn off from it by means of the siphon, and allowed to flow into the vessel B, in a very slender stream, which can be regulated by the glass stopcock; B has also been filled with sul-

phuric acid, and subsequently charged with pure dry chlorine by means of the bent tubes at *b*. C is a tube filled with dry chloride

FIG. 268.



of calcium; D, a tube filled with pumice moistened with sulphuric acid; E, a wide tube filled with nitrate of silver in crystals, immersed in a bath of oil; F, the receiver for the anhydrous nitric acid, which is kept cool by a freezing mixture of ice and salt. The tube E F is made of one continuous piece of glass, as the acid immediately attacks and destroys cork or caoutchouc joints: a portion of one of the lower oxides of nitrogen is liquefied and collects in the bulb in F, and is thus separated. The chlorine displaces the nitric acid and oxygen from the nitrate of silver; chloride of silver is formed, and the nitric anhydride and oxygen escape. By surrounding the receiver, F, with a freezing mixture, the nitric anhydride is condensed in crystals. The decomposition may be represented in the following manner, though it is probably not quite so simple* :—

$$\overbrace{AgO,NO_5}^{\text{Nitrate of silver.}} + Cl \text{ give } \overbrace{AgCl}^{\text{Chlor. silver.}} + O + \overbrace{NO_5}^{\text{Nitric anhydride.}}.$$

Deville ascertained the composition of nitric anhydride by

* Possibly a chloro-nitric acid is formed first, thus:—$AgNO_6 + 2\,Cl = AgCl + NO_4Cl + O_2$, and then this chloro-nitric acid decomposes a second atom of nitrate of silver; $AgNO_6 + NO_4Cl = AgCl + (NO_5)$

estimating the quantity of nitrogen which a given weight of the compound furnished after the oxygen had been removed from it by transmitting its vapours over finely divided metallic copper, which, at a high temperature, combines rapidly with the oxygen. 100 parts by weight of the anhydride were thus found to contain 25·9 of nitrogen; the deficiency, 74·1, is oxygen: or 14 parts of nitrogen are united with 40 of oxygen.

(305) *Common Impurities of the Acid.*—Hydrated nitric acid is liable to be contaminated with a variety of foreign matters, of which sulphuric acid, chlorine, potash, and oxide of iron are the most frequent. Its usual yellow or red colour is owing to the presence of some of the lower oxides of nitrogen. It should leave no fixed residue when evaporated on a slip of glass, and give no precipitate when, after dilution with three or four times its bulk of water, it is tested for sulphuric acid with nitrate of baryta, and for chlorine with nitrate of silver. It may readily be obtained free from all impurities, except the lower oxides of nitrogen, by distilling it a second time; if chlorine be present, nitrate of silver may be added so long as the silver salt occasions a precipitate; or a silver coin may be dissolved in the acid, after which the rectification may be proceeded with. The lower oxides of nitrogen may be removed by diluting the acid with water till of a sp. gr. not exceeding 1·42, and then distilling with 2 or 3 per cent. of bichromate of potash.

Nitrates.—Nitric acid is monobasic; that is to say, each atom of acid requires 1 atom of a base like potash to neutralize it; the salts which it forms are termed *nitrates.* These salts may be procured without difficulty by dissolving either the metal itself, or its oxide, or its carbonate, in nitric acid more or less diluted. Many of the nitrates, including those of potash, soda, oxide of ammonium, baryta, lead, and silver are anhydrous. Others combine with 6 atoms of water of crystallization; among these are the salts of magnesia, zinc, nickel, cobalt, protoxide of iron, and copper; whilst in others the proportion of the water is different, nitrate of lime retaining 4 Aq, and nitrate of strontia 5 Aq. If crystallized at a high temperature, nitrate of copper retains only 3 Aq, and nitrate of strontia may be obtained in the anhydrous form. No acid nitrates are known to exist, but several subnitrates may be procured; that is to say, salts may be formed which contain more than 1 atom of base for each atom of acid: such, for instance, as subnitrate of copper ($4\,CuO,NO_5+3\,HO$). Most of the nitrates fuse readily when heated: at an elevated temperature they are all decomposed, and in most cases the pure oxide of the

metal is left. When thrown on glowing coals, the nitrates are decomposed with scintillation; if paper be moistened with the solution of any nitrate, allowed to dry, and then burned, the smouldering combustion characteristic of touch-paper will be produced. This property is, however, also exhibited by the salts of some other acids, of which the chloric is the most important.

There is no ready method of precipitating nitric acid from its solutions, since all its compounds are dissolved by water more or less freely. Various indirect methods have been proposed for ascertaining its presence.* One of the best of these consists in neutralizing the solution, if acid, with potash, and evaporating nearly to dryness; then adding a few copper clippings, and heating the mixture with a little oil of vitriol: the copper, by combining with a portion of the oxygen of the nitric acid, decomposes the acid if present, and characteristic red fumes of peroxide of nitrogen show themselves. A quantity of these fumes too small to be visible may be rendered evident by suspending in the vessel a piece of paper moistened with a mixture of starch and solution of iodide of potassium, which will become blue from liberated iodine. A still

* The accurate quantitative determination of nitric acid when mixed with other acids is a matter of considerable difficulty. One method consists in the conversion of the acid into ammonia and the subsequent determination of the amount of ammonia found (311). Another, which, when the quantity of nitric acid is very small, furnishes excellent results, is that proposed by Pugh (*Q. J. Chem. Soc.*, xii. 35). It is based upon the determination of the amount of protochloride of tin which is converted into bichloride of tin when the solution is heated with nitric acid in presence of an excess of hydrochloric acid. A certain quantity of the concentrated solution containing the nitric acid to be determined is introduced into a strong tube, and a known volume of a solution of protochloride of tin in a large excess of hydrochloric acid is added, the strength of the tin solution having been ascertained, by the use of a standard solution of bichromate of potash. Care is taken to employ an excess of the tin solution. A fragment of marble is dropped into the tube so as to produce a quantity of carbonic acid sufficient to displace the atmospheric air. The tube is then carefully sealed and exposed for about a quarter of an hour to a temperature of 340°. It is allowed to cool, and the contents of the tube are next transferred to a glass and diluted with three or four ounces of water, a few drops of a weak solution of iodide of potassium and starch are then added, and the amount of tin still remaining in the form of protosalt is determined by the addition of a graduated solution of bichromate of potash, until the liquid become blue from the liberation of iodine. The reaction upon which this process depends may be thus expressed:—

$$HO,NO_5+8\,SnCl+9\,HCl=H_4NCl+8\,SnCl_2+6\,HO;$$

the nitric acid being wholly converted into ammonia during the operation. The difference between the amount of the bichromate originally required to peroxidize the quantity of the tin solution employed, and that actually consumed after the experiment is over, yields the data for fixing the quantity of nitric acid: 393·3 grs. of bichromate of potash represent 54 of nitric acid (NO_5).

smaller quantity of the acid may be detected by mixing a small quantity of a concentrated solution of green sulphate of iron with the liquor to be tested, and gradually allowing the oil of vitriol to flow into the solution so as to form a distinct stratum below it. In this case the characteristic action consists in the formation, at the line of contact between the two liquids, of a brownish-red solution, the colour of which disappears on boiling; the coloration depends upon the fact that the deutoxide of nitrogen which is formed by the deoxidizing action of one portion of the iron salt becomes dissolved, with the distinctive brown colour, in the solution of the unoxidized part of the salt; the deoxidation of the nitric acid which occurs may be represented in the following equation, omitting the water in the two acids:—

$$\overbrace{6\,(FeO,SO_3)}^{\text{Protosulphate of iron.}} + \overbrace{3\,SO_3}^{\text{Sulph. Acid.}} + \overbrace{NO_5}^{\text{Nitric Acid.}} = \overbrace{3\,(Fe_2O_3,\,3\,SO_3)}^{\text{Sesquisulphate of iron.}} + \overbrace{NO_2}^{\text{Deutox. nitrogen.}}$$

If a few drops of hydrochloric acid be added to a solution which contains free nitric acid, or a nitrate in solution, the liquid acquires the power of dissolving gold leaf. This effect, however, is produced by hydrochloric acid in solutions of the chlorates, bromates, and iodates; but the presence of these salts may be detected by other characters (321, 330, 333).

(306) PROTOXIDE OF NITROGEN, or *Nitrous Oxide*, ($NO=22$). *Sp. Gr.* 1·527; *Comb. Vol.* 2.—*Preparation.*—1. If nitric acid, diluted with 8 or 10 parts of water, be digested on metallic zinc, the metal deoxidizes the acid, and a colourless gas is slowly given off, composed of 1 atom of nitrogen united with 1 of oxygen.

2.—But to obtain the gas in a pure state it is far better to heat nitrate of ammonia (H_4NO,NO_5), (the salt furnished by neutralizing pure nitric acid with carbonate of ammonia) in a glass retort; the salt quickly melts, and at a temperature of between 400° and 500° apparently begins to boil, but in reality it is undergoing decomposition, by which it is entirely resolved into the gaseous protoxide of nitrogen and steam. The temperature must be carefully watched, and not be allowed to rise so high as to occasion the production of white vapours in the retort, because the decomposition is then apt to occur with explosive violence. The reaction may be explained as follows:—Ammonia is a compound of nitrogen with hydrogen; when the nitrate of ammonia is heated, the hydrogen of the ammonia combines with part of the oxygen of the nitric acid, forming water, whilst the nitrogen of the ammonia at the same time becomes oxidized at the expense of another part of the oxygen of the nitric

acid. The result is that the whole of the nitrogen, both of the nitric acid and of the ammonia, is liberated in the form of protoxide of nitrogen; thus:—

$$\underbrace{H_3N, HO, NO_5}_{\text{Nitrate of ammonia.}} \text{ becomes } 2\underbrace{NO}_{\text{Protox. nitrogen.}} + 4\underbrace{HO}_{\text{Water.}}$$

An ounce of the salt furnishes about 500 cubic inches of the gas.

3.—L. Smith adopts a modification of the foregoing process for preparing the gas: he decomposes sal ammoniac by means of nitric acid (of sp. gr. 1·20) at a gentle heat. The gas which is obtained in this manner is not pure, but is contaminated with small quantities of chlorine and of nitrogen; the chlorine may be removed by allowing the gas to bubble up through a solution of potash. Advantage may sometimes be taken of this action of nitric acid on sal ammoniac to destroy an excess of muriate of ammonia in solution in the course of an analysis.

Properties.—Protoxide of nitrogen is a transparent, colourless gas, with a faint sweetish smell and taste: 100 cubic inches of water at 32° dissolve 130 cubic inches of the gas; at 59°, 77 cubic inches; and at 75° only 60 cubic inches (Bunsen). Owing to this considerable diminution in solubility with the rise of temperature, it should be collected over warm water. Under a pressure of 50 atmospheres at 45°, it is reducible to a colourless liquid of sp. gr. at 45° of 0·908. It boils at about −126°, and may be frozen into a transparent solid at about −150°. When the liquid protoxide was mixed with bisulphide of carbon and exposed to evaporation *in vacuo*, Natterer obtained a reduction of temperature which he estimated at −220° F.; this is a lower point than has hitherto been attained by any other means. The gaseous protoxide of nitrogen has a specific gravity of 1·527, which coincides with that of carbonic acid. This gas possesses the qualities neither of an acid nor of an alkali. It supports the combustion of many bodies with a brilliancy resembling that which they exhibit when burned in oxygen. It is, however, at once distinguished from oxygen by its considerable solubility in water. A glowing match bursts into flame when plunged into the protoxide: sulphur when kindled burns in it with a pale rose-coloured flame.

Soon after the discovery of the protoxide of nitrogen, Davy ascertained that it may be respired for a few minutes: it then produces a singular species of transient intoxication, attended in many instances with an irresistible propensity to muscular exertion, and often to uncontrollable laughter; hence the gas has acquired the popular name of *laughing-gas*. Different individuals

are affected in different degrees and in various ways, according to the temperament of each. In plethoric persons, where there is any tendency to over-active circulation through the brain, the experiment is not a safe one. The intoxicating effects pass off in a few minutes, and frequently no recollection of what has passed is retained, and no lassitude is perceived after the extreme exertion. When the gas is to be respired, great attention to its purity is requisite; the nitrate of ammonia from which it is prepared must be perfectly free from hydrochloric acid, as otherwise a little chlorine might be liberated, which, if breathed, would be highly irritating to the lungs.

Composition.—If protoxide of nitrogen be passed repeatedly through a porcelain tube heated to bright redness, the gas is decomposed into a mixture of oxygen and nitrogen, 2 volumes becoming expanded permanently into the space of 3 volumes. An easy method of analysing the protoxide of nitrogen consists in mixing it with hydrogen, and passing an electric spark through the mixture. If 4 measures of protoxide of nitrogen be mixed with an excess of hydrogen gas, say with 6 measures of hydrogen, in the bent eudiometer (fig. 257), 10 measures of mixed gas will be produced; and on transmitting the electric spark, inflammation will occur; steam will be formed by the oxidation of the hydrogen, and will be immediately condensed; the 10 measures will thus be reduced to 6: but the quantity of oxygen contained in the protoxide of nitrogen cannot be at once inferred from this change of bulk: before this can be done it is needful to ascertain how much hydrogen is left in the mixture. This may be effected by mixing the 6 remaining measures with 2 measures of oxygen, thus making 8 measures, and again transmitting the electric spark. Steam will again be formed, and immediately condensed, the 8 measures of the mixture will now be reduced to 5; 3 measures of the gas will therefore have disappeared, two-thirds of which, or 2 measures, are hydrogen: 1 measure of the gas now left must consequently be oxygen which was added in excess, and the remaining 4 measures are nitrogen. Of the 6 measures of hydrogen originally added, 4 have therefore combined with oxygen derived from the protoxide; and since 4 measures of hydrogen require 2 measures of oxygen for conversion into water, the 4 measures of the protoxide must have contained 2 measures of oxygen. It appears, also, that protoxide of nitrogen contains its own bulk of nitrogen, since the 4 measures of the gas originally employed furnish 4 measures of nitrogen; this nitrogen is moreover so combined with 2 measures of oxygen, that the 6 measures of the two gases when

united have condensed into the space of 4 measures, or into two-thirds of the bulk which they occupied when separate. The specific gravity of the gas shows that this conclusion is correct, for 100 cubic inches are found by experiment to weigh between 47 and 48 grains, and by calculation we find that such should be the case, for—

	Grains.	By vol.	Sp. gr.
100 cub. in. of nitrogen weigh . . .	30·12	or 1·0	= 0·971
50 cub. in. of oxygen weigh	17·10	0·5	= 0·5528
They give 100 cub. in. of protoxide of nitrogen, and weigh	47·22	1·0	= 1·5238

The proportion of nitrogen contained in the gas may also be ascertained by means of potassium: for if potassium be heated in protoxide of nitrogen, it burns vividly, and is converted into potash, leaving a volume of nitrogen equal to that of the gas employed. The composition of this gas may therefore be thus represented:—

		By weight.		
Nitrogen	$N =$	14	or 63·64	2 vols.
Oxygen	$O =$	8	36·36	1 vol.
Protoxide of nitrogen	$NO =$	22	100·00	2 vols.

(307) Deutoxide, or Binoxide of Nitrogen; *Nitric Oxide*, (NO_2=30). *Sp. Gr.* 1·039; *Comb. Vol.* 4.—*Preparation.*—1. If nitric acid be diluted with twice its bulk of water, so as to reduce it to a specific gravity of about 1·2, and be poured upon copper clippings or metallic mercury placed in a retort, brisk action speedily occurs; a gentle heat, if necessary, may be applied until it commences; the retort becomes filled with red fumes, and a gas is disengaged, which if collected over water will be found to be colourless. During this decomposition, each atom of nitric acid loses 3 atoms of oxygen, and gives off 1 atom of deutoxide of nitrogen, the metal taking oxygen from one portion of the acid, and forming an oxide which combines with a portion of the undecomposed acid. The following equation shows the reaction which occurs between 3 atoms of copper and 4 of nitric acid, resulting in the formation of 1 atom of deutoxide of nitrogen and 3 atoms of nitrate of copper:—

$$\overbrace{3\,Cu}^{\text{Copper.}} + \overbrace{4\,(HO, NO_5)}^{\text{Nitric acid.}} = \overbrace{3\,(CuO, NO_5)}^{\text{Nitrate of copper.}} + \overbrace{NO_2}^{\text{Deutox. nitrogen.}} + \overbrace{4\,HO}^{\text{Water.}}$$

2.—The deutoxide may also be obtained perfectly pure by digesting hydrochloric acid with iron filings till it will dissolve no more, decanting the clear liquid, and adding to it its own bulk of hydrochloric acid: on placing the solution in a retort, and adding nitrate

of potash, the deutoxide of nitrogen is immediately evolved in large quantity (Pelouze). The reaction is not so simple as in the preceding case; it is represented as follows:—

$$\overbrace{6\,FeCl}^{\text{Protochlor. iron.}} + \overbrace{4\,HCl}^{\text{Hydrochlor. acid.}} + \overbrace{KO,NO_5}^{\text{Nitrate of potash.}} \text{ give } \overbrace{3\,(Fe_2Cl_3)}^{\text{Perchlor. iron.}} + \overbrace{4\,HO}^{\text{Water.}} + \overbrace{KCl}^{\text{Chlor. of potassium.}} + \overbrace{NO_2}^{\text{Deutox. of nitrogen.}}$$

A simple modification of this method consists in placing in a retort 1 ounce of commercial nitre, 8 ounces of protosulphate of iron, and pouring upon them half a pint of diluted sulphuric acid (1 ounce of acid to 3 ounces of water). Such a mixture will give nearly 400 cubic inches of pure deutoxide of nitrogen.

Composition.—The composition of the deutoxide cannot be ascertained by detonation with hydrogen; for equal volumes of hydrogen and of the deutoxide burn quietly with a green flame on the approach of a burning body. Davy analysed the deutoxide of nitrogen by heating charcoal strongly in it; 4 volumes of the gas by this treatment furnish 2 volumes of nitrogen, and 2 volumes of carbonic acid: but carbonic acid contains its own volume of oxygen; the deutoxide must therefore have consisted of 2 volumes of nitrogen united without condensation with 2 volumes of oxygen. The density of the gas confirms the correctness of this result, for by experiment 100 cubic inches weigh rather more than 32 grains, and by calculation,

	Grs.	By vol.	Sp. gr.
50 cubic inches of nitrogen weigh . . .	15·06 or	0·5 =	0·486
50 cubic inches of oxygen	17·10	0·5 =	0·552
100 cubic inches of binoxide of nitrogen .	32·16	1·0 =	1·038

Potassium burns when heated in the gas, potash being produced. If the experiment be conducted in such a manner as to allow the residual gas to be measured after the combustion is over, 4 volumes of the deutoxide will be found to leave 2 volumes of nitrogen. A similar result is obtained when tin is heated in the gas; consequently its composition may be thus represented:—

Nitrogen	$N = 14$ or	46·67	2 vols.
Oxygen	$O_2 = 16$	53·33	2 vols.
Deutoxide of nitrogen	$NO_2 = 30$	100·00	4 vols.

Properties.—Deutoxide of nitrogen has a strong disagreeable odour, and cannot be respired. It has hitherto resisted all attempts to liquefy it. Water does not dissolve more than $\frac{1}{20}$th of its bulk of this gas.

The deutoxide is the most stable of the oxides of nitrogen, and may be exposed to a red heat without undergoing decomposition;

but a succession of electric sparks converts it, if it be moist, into a mixture of nitrogen and hydrated nitric acid: and if digested upon moistened iron filings, or a moist sulphide of one of the alkaline metals, it is slowly converted into protoxide of nitrogen. Many burning bodies, such, for instance, as a lighted taper, or phosphorus just kindled, are extinguished when plunged into the gas; but a decomposition of the gas will be effected if the phosphorus be burning vigorously, and it will deflagrate with a brilliancy equal to that produced by its combustion in oxygen.

Deutoxide of nitrogen is completely absorbed by a solution of protosulphate of iron, with which it forms a deep reddish-brown liquid. All the salts of the protoxide of iron exert a similar action, and, according to Peligot, 4 equivalents of the salt of iron absorb 1 equivalent of the deutoxide, the solution in the case of the sulphate containing $4\ (FeO,SO_3)+NO_2$. The deep colour of the liquid thus formed is employed, as has already been mentioned (305), for the purpose of ascertaining the presence of nitric acid in solution. This brown liquid absorbs oxygen rapidly from the air or from gaseous mixtures; when heated, most of the deutoxide is expelled from it unchanged. Solutions of the salts of the protoxide of tin and of suboxide of mercury also absorb the deutoxide of nitrogen, but they undergo change, and the gas cannot again be expelled from them by heat. Nitric acid likewise rapidly absorbs the gas: if the acid be concentrated, the solution becomes reddish brown; if more diluted, it is green; if still weaker, the solution is blue, but if diluted below a specific gravity of 1·15, little of the gas is absorbed and the acid remains colourless.

The deutoxide of nitrogen is neither acid nor alkaline in its characters. It has, however, a very powerful affinity for oxygen, and to this circumstance is owing one of the most characteristic properties of the gas. When mixed with oxygen, or with any gas containing uncombined oxygen, dense red fumes are produced. These red fumes are freely soluble in water, and furnish an acid liquid. Formerly this circumstance was employed to determine the quantity of oxygen in mixture with other gases; but the method is now abandoned, as the absorption is not uniform, owing to the formation in uncertain quantity of a mixture of the soluble oxides of nitrogen. It may, however, be used with advantage as a qualitative test to demonstrate the existence of uncombined oxygen in a gaseous mixture.

(308) NITROUS ACID; or *Nitrous Anhydride* (formerly known as *Hyponitrous Acid*) $(NO_3)_2$ or $(NO_3=38)$. *Preparation.*—1. By mixing in an exhausted flask 4 volumes of deutoxide of nitrogen

with 1 volume of oxygen, both in a perfectly dry state, brownish-red fumes of nitrous acid are formed, which at a temperature of 0° F. become condensed into a blue very volatile liquid.

2.—Nitrous acid may also be obtained nearly in a state of purity, by heating in a capacious retort 1 part of starch with 8 parts of nitric acid, of sp. gr. 1·25: it may be dried by passing it over chloride of calcium, and may then be liquefied by transmission through a U-shaped tube surrounded by a mixture of ice and salt.

Properties.—Water immediately decomposes the anhydride into nitric acid and deutoxide of nitrogen: the presence of a small quantity of water converts the blue into a dark green liquid, but a larger quantity decomposes it with effervescence: nitric acid is formed, and deutoxide of nitrogen escapes. This reaction may be thus represented:—

$$2\,HO + 3\,(NO_3)_2 \text{ give } 2\,(HO,NO_5) + 4\,NO_2.$$

Though in its uncombined form nitrous acid is decomposed with such facility, yet it forms permanent compounds with the alkalies: these salts are called *nitrites*. If deutoxide of nitrogen be placed over a solution of caustic potash, and small quantities of oxygen be added, nitrite of potash is produced in the liquid; and if nitre, or nitrate of soda, be heated to redness until the gas which is evolved begins to contain nitrogen, the residue will be found to be composed chiefly of nitrite of potash or soda. These nitrites are soluble in alcohol, and may thus be separated from the corresponding nitrates, which are insoluble. The nitrites of potash and soda, and the monobasic nitrites of silver and lead, are anhydrous. If the nitrite either of potash or of soda be dissolved in water, and nitrate of silver be added, a sparingly soluble anhydrous nitrite of silver is precipitated: by dissolving this precipitate in hot water, it is obtained pure in crystals as the liquid cools. When a fragment of nitrite of potash is moistened with a solution of sulphate of copper, it produces a brilliant green solution of nitrite of copper, the colour of which is quite characteristic. The addition of cold diluted sulphuric acid to a solution of a nitrite decomposes the salt, and the liquid then becomes of a brownish-red colour on adding a solution of protosulphate of iron. The nitrites may thus be distinguished from the nitrates, since the latter do not change colour when similarly treated, unless heat be applied.

Acid solutions of the nitrites destroy the blue colour of indigo at ordinary temperatures; they bleach the permanganate of potash,

and slowly reduce bichromate of potash to a green salt of chromium. The terchloride of gold is reduced to the metallic form by these salts, and the subsalts of mercury give a grey precipitate of reduced mercury. A very minute trace of any nitrite may be detected by mixing a dilute solution of iodide of potassium, free from iodate, with starch and a little diluted hydrochloric acid (sp. gr. 1·006); the liquid to be tested, after being acidulated with hydrochloric acid, is then to be added to the test mixture, when the blue colour of iodide of starch will appear, even when only traces of a nitrite are present.

The presence of nitrites in the well waters of towns is of common occurrence, probably from the oxidation of the ammonia derived from animal matters in the soil. Nitrous acid is formed from ammonia, when the latter is in contact with atmospheric air in the presence of platinum black (823), or of a coil of heated platinum wire: if a coil of red-hot platinum wire be held in a jar of air moistened with a few drops of a strong solution of ammonia, white fumes of nitrate of ammonia will be formed. The contact of metallic copper is still more effectual in promoting the formation of nitrous acid from ammonia, when free oxygen is present: if a small quantity of pulverulent copper be shaken up in a bottle of air, with a few drops of a solution of ammonia, the oxygen will be absorbed in a few minutes, and nitrous acid will be found in the liquid. Even bright slips of copper effect a similar oxidation of the ammonia, whilst oxide of copper is formed simultaneously. The cause of these phenomena is obscure; they belong to the class of actions commonly known as catalytic (859, 861).

(309) PEROXIDE OF NITROGEN: *Hyponitric Acid* (formerly called *Nitrous Acid*), ($NO_4 = 46$).—*Comb. Vol.* 4; *Melting Pt.* 16°; *Boiling Pt.* 71°.—*Preparation.*—1. The red fumes which appear on mixing the deutoxide of nitrogen with atmospheric air consist mainly of peroxide of nitrogen; 2 volumes of oxygen and 4 volumes of the deutoxide of nitrogen in combining become condensed into the space of 4 volumes; hence its specific gravity should be 1·591. Mitscherlich found it by experiment to be 1·70.

			By weight.		By volume.			Sp. gr.
Nitrogen	N	=	14	or 30·44	2	or 0·5	=	0·486
Oxygen	O_4	=	32	69·56	4	1·0	=	1·105
Peroxide of nitrogen	NO_4	=	46	100·00	4	1·0	=	1·591

Peroxide of nitrogen may be procured in prismatic crystals by passing 4 volumes of the deutoxide and 2 volumes of oxygen, both perfectly dry, into tubes previously dried with scrupulous care, and cooled down by a mixture of ice and salt. (Péligot, *Ann. de Chimie,* III. ii. 61.) These crystals melt at 16° F.; at the ordinary temperature of the air they form an orange-coloured liquid, which boils at 71°, and produces a deep red vapour. It is remarkable that after this compound has once been melted it does not freeze even at 0°. This substance is decomposed by water with singular facility; a minute trace of water is sufficient to prevent the formation of the crystalline compound, occasioning in its stead the production of a green liquid, probably $NO_3,NO_5 + Aq$, similar to that obtained by the distillation of nitrate of lead. The peroxide of nitrogen was long considered to possess acid properties, and hence was termed nitrous acid. It, however, does not enter into combination with bases, but is immediately decomposed by them into nitric and nitrous acids:—

$$2\ NO_4 + 2\ (KO,HO) \text{ yielding } KO,NO_5 + KO,NO_3 + 2\ HO.$$

Much speculation has been indulged in as to its probable composition. Berzelius latterly was disposed to regard this compound as a combination of nitric acid with deutoxide of nitrogen; $3\ NO_4$ being represented as $(NO_2, 2\ NO_5)$.

2.—If nitrate of lead be dried, and heated strongly in a small glass retort, it is decomposed; deep red fumes, consisting of a mixture of peroxide of nitrogen and free oxygen, are produced, and oxide of lead is left; PbO,NO_5 yielding $PbO + O + NO_4$. If the red vapour be made to pass through a bent tube surrounded by ice and salt, as shown in fig. 269, the peroxide is condensed to a liquid which is green, owing to the presence of a little moisture. Towards the latter part of the distillation the anhydrous peroxide comes over, and if the receiver be changed, it may be obtained in crystals, which are the same as those produced by the mixture of dry oxygen and deut-

FIG 269.

oxide of nitrogen; the minutest trace of moisture, however, converts them into the liquid form. This liquid is nearly colourless at 0°; it becomes yellow at 14° F., and at ordinary temperatures is red. It has a specific gravity of 1·451, boils at 82°, and freezes at −40°. It emits a dense red vapour, which becomes deeper in tint as the temperature rises, till at 100° it is almost opaque. This vapour has a peculiar, suffocating odour. It supports the combustion of a taper, and of many burning bodies. If water be gradually added to the liquid peroxide it passes through various tints, becoming successively orange, yellow, green, blue, and finally colourless, an effervescence being occasioned during the whole time from the escape of deutoxide of nitrogen; finally, nitric acid in abundance is formed in the liquid. The reaction may be traced as follows:—

$$2\ HO + 3NO_4 = NO_2 + 2\ HO, NO_5$$

The deutoxide of nitrogen, on mixing with the oxygen of the air, reproduces the peroxide of nitrogen as usual. The different tints assumed by the liquid during dilution appear to be owing to the solution of the deutoxide of nitrogen in varying proportion in the nitric acid produced by the decomposition.

Peroxide of nitrogen may be distinguished from nitrous acid by its power of imparting to a neutral solution of sulphocyanide of potassium a red tint closely resembling that produced in the same reagent by the persalts of iron; an excess of the peroxide, however, again renders the liquid colourless (Hadow).

(310) The important influence of proportion upon the products of chemical combination is exhibited in a striking light by these compounds of nitrogen with oxygen. The same elements, according to the quantities in which they are united, may, as in nitric acid, produce one of the most corrosive compounds in the range of chemistry; or may give rise, as in the case of the protoxide of nitrogen, to a stimulating and intoxicating gas, which may be breathed with impunity; while the intermediate combinations exhibit properties entirely different from either. A broad distinction may also be easily traced between the results of mixture and those of true chemical union. The properties of the atmosphere are the results of simple admixture; the chemical qualities of oxygen appearing to be simply diluted by its apparently inert companion, nitrogen (just as the sweetness of sugar is reduced by the addition of water); whilst each one of the true combinations of nitrogen with oxygen exhibits characters distinct from those of either of its components.

§ II.—Compounds of Nitrogen with Hydrogen.

Ammonia, *Volatile Alkali, or Spirit of Hartshorn* ($H_3N=17$.)
Sp. Gr. 0·59; *Comb. Vol.* 4.

(311) This important compound has received the name of ammonia, from the circumstance of its having been obtained from a salt termed sal ammoniac, first procured in Libya, near the temple of Jupiter Ammon. Nitrogen and hydrogen do not combine directly with each other; nevertheless, their indirect combination is a circumstance of continual occurrence. The spontaneous decomposition of moist animal matters, which contain both hydrogen and nitrogen, and almost every process of oxidation in the presence of moisture, is attended with the formation of ammonia. The hydrogen, at the moment of its liberation from the water by deoxidation, appears to enter into combination with the nitrogen of the atmosphere, which, to a small extent, is held in solution, and thus ammonia is formed. Moistened iron filings, if exposed to the air, become rusty, and the oxidized compound retains a small quantity of ammonia. The deoxidation of dilute nitric acid by the metals also frequently gives rise to the production of ammonia; both nitrogen and hydrogen are liberated simultaneously, a part of the water undergoing deoxidation at the same time that the acid is decomposed. Tin, zinc, and iron exhibit this effect in a marked degree.

This reaction has been used as a means of estimating the quantity of nitric acid in solutions; for by dissolving zinc very slowly in diluted hydrochloric acid, and adding the nitric solution in small quantities at a time, the whole of the nitric acid is converted into ammonia. (Nesbit, *Q. J. Chem. Soc.*, i. 681.) When a mixture of 2 volumes of deutoxide of nitrogen and 5 of hydrogen is transmitted over spongy platinum or platinized asbestos (859) gently heated, water and ammonia are produced. Hadow has also observed the formation of ammonia when nitrous acid or peroxide of nitrogen are reduced by transmitting them through a solution of hydrosulphate of sulphide of potassium (KS, HS) or through one of protacetate of iron.

Ammonia exists in minute quantity in the atmosphere.* It is

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* According to the elaborate researches of Ville, which appear to have been conducted with every precaution to ensure accuracy, 10,000,000,000 parts of air contained on the average, in the year 1851, 237 parts by weight of ammonia, and in 1852, 210 parts. This amounts to about one volume of ammonia in twenty-eight million volumes of air: other experimenters make the quantity

also found in clayey and in peaty soils, both of which absorb it freely. For the purposes of manufacture it is, however, always procured by the distillation, in closed vessels, of organic matters containing nitrogen. During the distillation of bones, and of animal refuse generally, ammonia in considerable quantity is formed, and condensed along with the fœtid products of the operation. But the principal part of the ammonia used in this country is obtained from the refuse products of the distillation of coal for the manufacture of gas. Amongst these products are water, and a considerable quantity of carbonate and hydrosulphate of ammonia; the ammoniacal salts become dissolved in the water, and constitute the ammoniacal liquor of the gas-works; this liquor is saturated with sulphuric or with hydrochloric acid, and thus the sulphate or muriate of ammonia of commerce is procured (514).

Preparation.—If equal weights of quicklime and either of the salts last named be separately powdered and intimately mixed, the powder, on being transferred to a retort and gently heated, gives off abundance of pure ammonia, as a transparent, colourless gas, of the peculiar, pungent odour of smelling salts. The lime combines with the acid and sets the ammonia at liberty; the result when muriate of ammonia is used being as follows:—

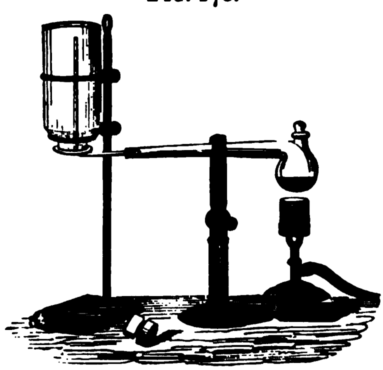
$$\overbrace{CaO}^{\text{Lime.}} + \overbrace{H_3N, HCl}^{\text{Mur. ammonia.}} = \overbrace{CaCl}^{\text{Chloride calcium.}} + \overbrace{H_3N}^{\text{Ammonia.}} + \overbrace{HO.}^{\text{Water.}}$$

Properties.—Ammonia produces a flow of tears from the eyes; it has an acrid taste, and, when breathed in a concentrated form, is fatal to life, from its irritating effects on the lungs. In a more

considerably higher. The proportion of ammonia contained in rain water is liable to considerable variation: in 1,000,000 parts of rain water collected in Paris during the last five months of 1851, Barral found 3·49 parts; Boussingault, at Liebfraunberg, in 1852, found only 0·744 parts; and Lawes and Gilbert, at Rothamsted, in 1853 and 1854, found the average amount from March to August to be 1·142, from September to February, 0·927 parts: the average of the two last determinations would give about 1 grain of ammonia in 14 gallons of rain water. Boussingault has corroborated Barral's results by experiments upon the rain collected in Paris; indeed it is not surprising that in a populous city, crowded with animal life, and with the exuviæ of animals, the proportion of ammonia in its atmosphere should be much higher than in the surrounding districts. It appears, also, that a larger quantity of ammonia is always contained in the water that is collected at the commencement of a shower than at the end of it, and more after a drought than after a period of rainy weather. In the water of dews and fogs, also, the amount of ammonia was found to be much higher than in rain water. The proportion of ammonia in water derived from the atmosphere is, in short, greater, the smaller the fall, a circumstance which is easily accounted for by the high solubility of the gas in water. The atmospheric supply of ammonia is intimately connected with the storing of nitrogen in plants.

diluted form it is a highly valuable stimulant. Ammonia does not support the flame of burning bodies, but is feebly combustible; a jet of the gas directed across the stream of hot air issuing from a lighted argand lamp, burns with a very pale green flame. If the gas be mingled with an equal bulk of oxygen, the mixture may be detonated by means of the electric spark; water, nitrogen, and traces of nitric acid are formed. If a mixture of ammonia and air or oxygen be passed over spongy platinum, water and nitric acid are amongst the products. Ammonia is extremely soluble in water, and must therefore be collected either over mercury, or by displacement, in the manner shown in fig. 270. The latter mode of collecting it may easily be effected, as the gas has little more than half the density of atmospheric air, its sp. gr. being only 0·59. Ammonia has a powerfully alkaline reaction, and turns turmeric paper brown. When collected by displacement, the gas must be allowed to pass into the bottle until a piece of dry turmeric paper held to the mouth of the bottle is immediately turned brown; the tube is then withdrawn, and the stopper, slightly greased, is inserted.

FIG. 270.



Ammonia neutralizes the most powerful acids, and forms a very important class of salts. Any volatile or gaseous acid brought into an atmosphere containing ammonia, produces a white cloud, owing to the formation of a solid salt. The property is often employed to detect small quantities of ammonia: quicklime or potash is mixed with the solution suspected to contain ammonia, and the whole gently warmed in a tube; a rod moistened with hydrochloric acid diluted with half its bulk of water is then placed in the upper part of the tube or vessel, and if ammonia be present, white fumes appear, even when the quantity of ammonia is too small to be distinguished by the smell. When ammoniacal gas is required in a state free from moisture it must be transmitted over quicklime, not over chloride of calcium; for this salt, as well as many other saline compounds, absorbs ammonia and forms with it a definite compound (518).

Ammoniacal gas may be liquefied by exposure to a cold of

$-40°$ F., or still more readily by generating it under the pressure of its own atmosphere. The easiest method is the following:—Chloride of silver in powder is exposed to a current of dry ammoniacal gas; the ammonia is rapidly absorbed, and the chloride increases in weight more than one-third. This substance is placed in one limb of a strong tube (182) bent to an obtuse angle, and then hermetically sealed; on applying heat to the chloride, and cooling the other end of the tube with a freezing mixture, the ammonia is condensed as a colourless liquid, which boils at $-29°$, exerts a pressure of 6·9 atmospheres at 60°, and has a specific gravity of 0·731 at 60° (Faraday; or 0·614, Andreeff). By a cold of $-103°$ it is frozen to a white, translucent, crystalline solid, which is denser than the liquid. The chloride of silver reabsorbs the liquefied ammonia at ordinary temperatures, and slowly reproduces the original compound.

Composition.—The composition of ammonia may be ascertained as follows:—If the dry gas be subjected to a succession of electric sparks, by the aid of Ruhmkorff's coil, or if it be passed slowly through a porcelain tube containing iron or copper turnings, heated to bright redness, the gas is decomposed; it becomes dilated to double its volume; 4 volumes of ammonia become 8; and the gas produced may be shown, by detonating a portion of it with oxygen, to consist of a mixture of 2 volumes of nitrogen with 6 volumes of hydrogen. If, after mixing 8 measures in the bent eudiometer with 4 of oxygen, so as to make 12 measures in the whole, the electric spark be transmitted, 3 measures will be left, owing to the formation of steam and its subsequent condensation. Since in the formation of water 2 measures of hydrogen combine with 1 measure of oxygen, one third of the volume of gas which has disappeared, or 3 measures, will be oxygen, and two thirds, or 6 measures, will be hydrogen. On agitating the residual gas with a solution of potash, no change of bulk will occur, consequently no carbonic acid can have been formed; but on the addition of pyrogallic acid (*note*, p. 54) to the gas whilst still in contact with the alkaline liquid, the excess of oxygen will be absorbed. This will amount to 1 measure, whilst 2 measures of nitrogen remain unacted upon; 2 measures of nitrogen must therefore have been present in the ammonia in combination with the 6 of hydrogen which have become condensed as steam; consequently, since the ammonia doubles its volume when decomposed by heat, the 4 volumes of ammonia must have been formed by 6 volumes of hydrogen, and 2 of nitrogen, condensed into half their bulk. The composition of ammonia may therefore be thus represented:—

			By weight.		By vol.		Sp. gr.
Hydrogen	H_3	= 3	or 17·65	6	or 1·5	=	0·1036
Nitrogen	N	= 14	82·35	2	0·5	=	0·4860
Ammonia	H_3N	17	100·00	4	1·0		0·5896

Other striking proofs of the composition of ammonia are afforded by the action of heat upon some of its salts. The decomposition of nitrate of ammonia offers one of these: by the action of heat, as already explained (306), the nitrate of ammonia (H_3N, HO, NO_5) is decomposed into water and protoxide of nitrogen, 4 HO + 2 NO; the 3 equivalents of hydrogen in the ammonia combining with 3 of oxygen in the nitric acid, and leaving the nitrogen of the ammonia to combine with deutoxide of nitrogen derived from the nitric acid. If a solution of the nitrite of ammonia (H_3N, HO, NO_3) be heated, the salt is decomposed, water and pure nitrogen are liberated: the result may be thus represented; H_3N, HO, NO_3=4 HO + 2 N; the hydrogen of the ammonia is in this case exactly sufficient to combine with the oxygen of the nitrous acid, forming water: this is an excellent mode of obtaining pure nitrogen.* Chlorine also decomposes ammonia at ordinary temperatures, and liberates nitrogen gas. Under certain circumstances it produces the detonating compound known as chloride of nitrogen (325). Bromine and iodine likewise decompose ammonia, and form similar detonating compounds, without producing any liberation of nitrogen.

(311*a*) *Solution of Ammonia.*—A solution of ammonia in water is a reagent continually required in the laboratory. When ammoniacal gas is passed into water it is rapidly absorbed, with considerable extrication of heat; at a temperature of 32°, Carius found that water takes up about 1050 times its volume of the gas; at 59°, 727 times its volume; and at 77°, 586 times its volume: water saturated with ammonia at 60° contains more than one-third of its weight of the gas, increasing in bulk nearly one-half, and becoming specifically lighter. The following table indicates the strength of solutions of pure ammonia of different specific gravities:—

* When nitrogen is to be procured in this way, the most convenient method consists in preparing nitrite of potash by saturating a solution of potash, of sp. gr. 1·38, with nitrous acid disengaged by acting upon starch with nitric acid of sp. gr. 1·25. This solution, if it be left slightly alkaline, may be preserved without alteration. When it is wanted for the preparation of nitrogen, the liquid is to be mixed with three times its bulk of a saturated solution of sal ammoniac, and gently heated in a small retort: nitrogen is evolved abundantly, and with great regularity (Corenwinder).

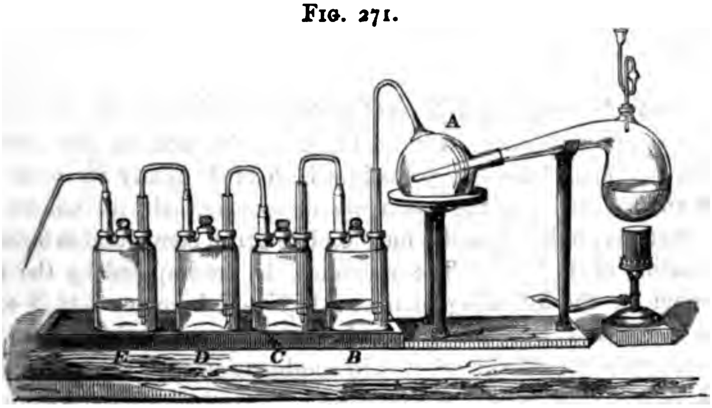
Strength of Solutions of Ammonia at 57° F. (Carius).

Ammonia in 100 parts by weight.	Specific gravity.	Ammonia in 100 parts by weight.	Specific gravity.	Ammonia in 100 parts by weight.	Specific gravity.	Ammonia in 100 parts by weight.	Specific gravity.
36	0·8844	27	0·9052	18	0·9314	9	0·9631
35	0·8864	26	0·9078	17	0·9347	8	0·9670
34	0·8885	25	0·9106	16	0·9380	7	0·9709
33	0·8907	24	0·9133	15	0·9414	6	0·9749
32	0·8929	23	0·9162	14	0·9449	5	0·9790
31	0·8953	22	0·9191	13	0·9484	4	0·9831
30	0·8976	21	0·9221	12	0·9520	3	0·9873
29	0·9001	20	0·9251	11	0·9556	2	0·9915
28	0·9026	19	0·9283	10	0·9593	1	0·9959

Solution of ammonia is colourless and intensely alkaline; it has an acrid, caustic taste, and blisters the skin if applied to it in a concentrated form; it freezes at about —40° F., yielding a gelatinous mass, destitute of odour. Simple exposure of the solution at ordinary temperatures to the air is attended with an escape of the gas, which occasions the pungent smell of the liquid. By heat the ammonia is rapidly expelled with the appearance of ebullition, thereby furnishing a ready extempore method of procuring the gas. By boiling the liquid for some time, the whole of the ammonia may be driven off, so that nothing but water is left in the retort.

Solution of ammonia is prepared on the large scale by mixing together in a capacious retort equal weights of well-burned quicklime and sal ammoniac; the lime is slaked and made into a paste with water before mixture. The retort is then connected with a series of bottles similar to those used for condensing nitric acid. If the operation be conducted on the small scale in the laboratory, the arrangement shown in fig. 271 may be adopted. The three-

FIG. 271.



necked bottles, B, C, D, E, are known by the name of Woulfe's bottles; in the globe, A, a small quantity of water is placed, to retain any solid particles which may be mechanically carried over by the gas; in the first bottle, B (which may be kept cool by immersion in cold water), a quantity of water equal in weight to that of the sal ammoniac used is introduced, taking care that it shall not fill more than half the capacity of the bottle, whilst the second contains water to condense any gas that may escape through the first. Each bottle is provided with a safety tube open at both ends, so that if the gas were absorbed in B, for example, more rapidly than it was supplied, instead of the liquid being driven back from the bottle, C, air would enter by the safety tube, and the equilibrium would be restored. The tube which delivers the gas passes down through the safety tube and projects a little beyond its lower opening, so that the gas rises in bubbles through the liquid and collects in the bottle; an air-tight joint, which can be mounted and dismounted immediately, is thus obtained.

Solution of ammonia, if pure, should, when evaporated, leave no solid residue; the presence of carbonic acid may be detected by lime water, which it renders milky; that of chlorine by neutralizing with pure nitric acid, and adding nitrate of silver, when it gives a white cloud; that of sulphuric acid by a white precipitate with nitrate of baryta after dilution and saturation with nitric acid; that of lime by a white precipitate on adding oxalate of ammonia; and that of copper or lead derived from the apparatus, by a black or brown precipitate or cloud with sulphuretted hydrogen. Lead in small quantity is a very frequent impurity in the commercial solution; it is usually derived from the action of the ammonia on the flint-glass bottles in which it is often improperly kept.

Alcohol also dissolves ammonia in abundance.

The salts of ammonia will be described with those of the other alkalies.

(312) AMIDOGEN ($H_2N=16$).—Ammonia is the only compound of hydrogen and nitrogen that has been obtained in the isolated form. When, however, potassium is heated gently in perfectly dry ammoniacal gas, the ammonia disappears, half its volume of hydrogen is produced, and a fusible, olive-green compound is formed, consisting of K,H_2N. The ammonia is decomposed by the potassium in the following manner: H_3N+K becomes KH_2N+H. The compound H_2N has received the name of *amidogen*, and it appears to be capable of existing in combination with several metals, and with a variety of bodies derived from the organic kingdom.

Compounds of this class have received the name of *amides*; they will be more conveniently examined hereafter (1045).

AMMONIUM ($H_4N=18$).—This compound, as is the case with amidogen, has not been obtained in a separate form. All the usual salts of ammonia, however, appear to contain it. Nitrate of ammonia, for example, consists not simply of H_3N, NO_5, but in addition contains an equivalent of water, which cannot be expelled by heat without the entire decomposition of the salt; this nitrate is therefore looked upon as a nitrate of oxide of ammonium, H_4NO, NO_5. Sal ammoniac is on this view regarded as chloride of ammonium, H_4N, Cl. The full discussion of the grounds upon which this theory rests will be best postponed till we enter upon a description of the salts of ammonia (507 *et seq.*).

CHAPTER VI.

THE HALOGENS.

BEFORE proceeding to notice some other compounds of the four elements already described, it will be desirable to examine the other non-metallic simple substances. We pass on therefore to a group of four closely allied bodies, viz., chlorine, bromine, iodine, and fluorine. These elements are characterized by the powerful activity of their affinities for other substances at the ordinary temperature of the air; and consequently none of them are found in an uncombined state. They form with the metals compounds analogous to sea-salt, and have been termed *halogens*, or salt-producers (from ἅλς, 'the sea').

§ I. CHLORINE (Cl=35·5); *Calcd. Sp. Gr.* 2·453; *Observed*, 2·47; *Comb. Vol.* 2.

(313) CHLORINE, the most important member of the group of halogens, is abundantly met with in combination with sodium, with which it constitutes ordinary table salt. This necessary of life occurs plentifully in beds in various parts of the world, and is the most abundant of the saline bodies contained in the waters of the ocean.

Properties.—Chlorine is a transparent gas of a greenish-yellow colour (whence the name is derived, from χλωρὸς, 'green,') and of a powerful suffocating odour, producing, if breathed, even

when largely diluted with air, distressing irritation of the air passages, attended with coughing. It is much heavier than air, 100 cubic inches weighing between 77 and 78 grains. Under a pressure of 4 atmospheres at 60°, it is condensed to a yellow, limpid liquid, of specific gravity 1·33; it does not conduct electricity, and remains unfrozen even at the cold of —220°. Chlorine is soluble in about half its bulk of cold water; this solution, which is readily formed by agitating the gas and water together, has the colour, odour, and astringent taste of the gas. According to Schönfeld, water at 50° dissolves 2·585 times its bulk of the gas; at 59°, 2·368, and at 104°, 1·365 times its bulk. Chlorine, in consequence of this solubility, cannot be advantageously collected over cold water. Mercury is acted upon by the gas with great rapidity. It is necessary, therefore, either to use warm water in the pneumatic trough, or to receive the gas by the process of displacement in dry bottles. With water, chlorine forms a definite *hydrate* ($Cl + 10\,HO$), which crystallizes at 32°; if it be enclosed in hermetically sealed tubes, it furnishes a ready method of obtaining liquefied chlorine, since it is easily decomposed by a gentle heat into water and free chlorine; the latter amounts to about one-fourth of the volume of the liquid.

Chlorine is not combustible, and it does not combine directly with oxygen. A taper burns in it with a reddish, smoky flame, the hydrogen of the combustible vapour of the wax combining with the chlorine, whilst part of the carbon, for which its affinity is but small, is deposited. Many bodies, however, take fire spontaneously when introduced into chlorine; this is the case with phosphorus: many of the metals in a finely divided state do the same; among them are copper leaf, finely powdered antimony, and arsenic. A great number of organic substances rich in hydrogen are decomposed by chlorine, sometimes with such rapidity as to inflame them; a bit of paper dipped into oil of turpentine and plunged into the gas bursts into flame, and deposits an abundance of a black carbonaceous compound.

The action of chlorine upon bodies containing hydrogen is often of a very peculiar kind. It combines with part of the hydrogen and withdraws it from the combination; each equivalent of hydrogen uniting with an equivalent of chlorine, and forming a powerful acid, the hydrochloric (HCl); whilst at the same time for each equivalent of hydrogen so withdrawn from the original compound, an equivalent of chlorine is substituted. It is in this way that chlorine exerts those bleaching powers which have rendered so essential a service to the calico-printer and the

paper-maker. Most of the vegetable colouring matters contain hydrogen, and are decomposed by chlorine, whilst colourless, or nearly colourless, compounds containing chlorine are formed instead of the coloured compounds with hydrogen. If a solution of chlorine be mixed with some of the blue liquid formed by dissolving indigo in sulphuric acid, or with ordinary writing ink, or with tincture of litmus, the colour will in each case be immediately and almost completely discharged, and it cannot be subsequently restored.

Another property of chlorine of great value is its disinfecting power,—by which is meant its power of destroying noxious vapours and miasmata; with this view it is frequently employed for fumigating buildings after the occurrence of contagious diseases.

Preparation.—1. Chlorine may be easily prepared from a mixture of 7 parts by weight of vitriol, previously diluted with 7 parts of water, and allowed to cool, and 4 parts of pounded chloride of sodium mixed intimately with 3 parts of finely pulverized black oxide of manganese. The decomposition may be represented as follows:—

$$\overbrace{MnO_2}^{\substack{\text{Oxide}\\ \text{mang.}}} + \overbrace{NaCl}^{\substack{\text{Chlor.}\\ \text{sodium.}}} + \overbrace{2\,(HO,\,SO_3)}^{\text{Sulph. acid.}} = \overbrace{MnO,\,SO_3}^{\substack{\text{Sulph.}\\ \text{mangan.}}} + \overbrace{NaO,\,SO_3}^{\text{Sulphate soda.}} + \overbrace{2\,HO}^{\text{Water.}} + \overbrace{Cl}^{\text{Chlorine.}}$$

The gas comes off slowly in the cold, but freely on the application of a gentle heat. A little hydrochloric acid is always formed in the reaction; this acid is easily removed from the chlorine by allowing the gas to bubble up through a vessel containing water, in the manner shown in fig. 266, where a similar apparatus is employed for carbonic oxide.

2. The manufacture of chlorine is practised on an enormous scale in the preparation of bleaching powder, or chloride of lime. It is generally prepared in capacious stills, sufficiently large to hold 200 gallons of liquid; these are sometimes made of lead, but more frequently of Yorkshire flags clamped together with ironwork, and the joints rendered tight by vulcanized caoutchouc. The lower part of these stills is enclosed in a case through which a current of steam is transmitted. Hydrochloric acid in solution, of specific gravity from 1·160 to 1·170 (which is obtained as a waste product in the manufacture of carbonate of soda from sea salt), is run through a curved funnel into the stills, which are charged with oxide of manganese in small lumps. Chloride of manganese is formed, and free chlorine is liberated in abundance; the reaction is illustrated by the following symbols:—

$$\underbrace{MnO_2}_{\text{Oxide mangan.}} + \underbrace{2HCl}_{\text{Hydrochlor. acid.}} \text{ produce } \underbrace{MnCl}_{\text{Chlor. mangan.}} + \underbrace{2HO}_{\text{Water.}} + \underbrace{Cl.}_{\text{Chlorine.}}$$

This process may also often be resorted to on the small scale in the laboratory with advantage. Three ounces of powdered oxide of manganese with half a pint of the commercial muriatic acid diluted with 3 ounces of water, will yield between 3 and 4 gallons of the gas. Care must be taken not to use an acid more dilute than 1·15 in the preparation of the gas; since, owing to a neglect of this precaution, explosions have in some instances occurred in operating on the large scale: hypochlorous acid, or one of the lower explosive oxides of chlorine, was probably formed in these cases.

Uses.—Besides the application of chlorine on the large scale in bleaching, it is frequently employed for disinfecting purposes. In the laboratory it is in continual requisition as an oxidizing agent; owing to its affinity for hydrogen it readily decomposes water, and liberates oxygen, which at the moment that it is set free enters readily into combination. The preparation of chlorate of potash (321), of ferric acid (638), and of the peroxides of cobalt and nickel (604, 613), affords illustrations of this mode of employing it: and, in researches upon the nature of many compounds furnished by organic chemistry, it often, as in the series of compounds obtained from Dutch liquid (400), is used as a means of throwing light upon their molecular constitution.

Chlorides.—Chlorine combines with all the non-metallic elements, and forms with many of them compounds of great importance; it also enters into combination with all the metals, and it combines directly with a large number of them, with the usual phenomena of combustion; the compounds which it forms are termed *chlorides*. With the exception of the chloride of silver and the subchlorides of mercury and copper, they are all more or less soluble in water. It frequently happens that chlorine combines with the same metal in more proportions than one: for example, with iron a protochloride ($FeCl$) and a sesquichloride (Fe_2Cl_3) may be formed; with platinum a protochloride ($PtCl$) and a bichloride ($PtCl_2$) may be obtained; and generally, for each oxide of the metal which is capable of uniting with acids to form salts, a corresponding chloride exists (444).

Chlorine when in solution in the uncombined form is easily recognised by its odour and its bleaching properties. Both when free, and when combined with a metal, it gives, on the addition of a solution of nitrate of silver, a curdy, flocculent, white precipitate,

which changes to violet on exposure to light; this white precipitate consists of chloride of silver, and is easily re-dissolved by adding a small quantity of solution of ammonia, but it is insoluble in nitric acid. Nitrate of suboxide of mercury also gives a white precipitate of subchloride of mercury in solutions of the metallic chlorides; the calomel (Hg_2Cl) thus formed is insoluble in cold diluted nitric acid, and is instantly blackened by the addition of a few drops of ammonia.

(314) HYDROCHLORIC ACID: *Muriatic Acid* ($HCl=36{\cdot}5$); *Sp. Gr.*, 1·2474; *Comb. Vol.*, 4.—The most important of the compounds which chlorine forms with the non-metallic elements is that obtained by its combination with hydrogen. The two gases may be mixed in equal volumes, and they will remain without action upon each other, if kept in the dark; but the moment that they are brought into direct sun-light they unite with a powerful explosion, and a colourless, intensely acid gas is the product. In diffused daylight the combination takes place gradually; but the application of a lighted match, or the passage of the electric spark through the mixture, instantly determines its explosion. Two volumes of chlorine unite thus with 2 volumes of hydrogen, producing 4 volumes of hydrochloric acid; no condensation therefore occurs in the act of union. The composition of hydrochloric acid is consequently the following:—

		By weight.		By vol.		Sp. gr.
Chlorine	Cl	= 35·5	or 97·26	2	or 0·5	= 1·2265
Hydrogen . . .	H	= 1·0	2·74	2	0·5	= 0·0345
Hydrochloric acid	HCl	= 36·5	100·00	4	1·0	= 1·2610

So powerful is the affinity of chlorine for hydrogen, that if either a solution of chlorine in water, or the gas itself in a moist state, be exposed to the sun's rays, water is decomposed, hydrochloric acid is formed, and the oxygen of the water is liberated: in the dark, however, chlorine has no power to decompose water.

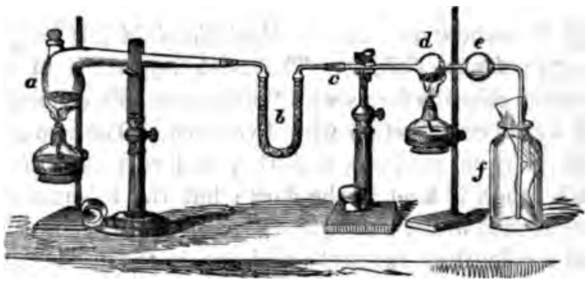
If moist chlorine be transmitted through a red-hot porcelain tube, hydrochloric acid is formed, and oxygen is set free; though, on the other hand, when hydrochloric acid gas is mixed with air and transmitted through an ignited porcelain tube chlorine is liberated and water is produced.

The composition of hydrochloric acid may be analytically determined by heating sodium in a measured volume of the gas. The metal burns vividly, and liberates a quantity of hydrogen equal in bulk to that of half the gas employed; common salt is formed at the same time. Analogous results are obtained if

iron or tin be substituted for sodium; chloride of iron or of tin being formed, whilst hydrogen is set at liberty.

The presence both of hydrogen and of chlorine in the acid gas is easily shown by the following experiment (Graham):—A quantity of hydrochloric acid is liberated from fused chloride of sodium by oil of vitriol, contained in the retort, *a*, fig. 272, and is dried by

FIG. 272.



being passed through a tube, *b*, filled with chloride of calcium: this tube is connected by vulcanized caoutchouc, *c*, with a tube upon which two bulbs have been blown: in the first of these, *d*, some pounded anhydrous black oxide of manganese is placed: a piece of litmus paper inserted in the bottle, *f*, which receives the escaping gas, is quickly reddened. On applying heat to the bulb, *d*, containing the oxide, chloride of manganese is produced, and not being volatile, it remains in the bulb, whilst water is formed and becomes condensed in the second bulb, *e*; in the meantime free chlorine passes on into the bottle, *f*, showing itself by its peculiar colour and its bleaching effect upon the litmus paper. The reaction has already been explained, and may be represented by the following symbols:—

$$2\ HCl + MnO_2 = 2\ HO + MnCl + Cl.$$

Preparation.—Hydrochloric acid gas is easily procured by placing fragments of common salt (which has been fused in a crucible at a red heat and allowed to cool) into a glass retort, and pouring over it twice its weight of oil of vitriol. Abundance of hydrochloric acid gas escapes; it must be collected either over mercury or by displacement of the air from dry bottles. In this case the water of the oil of vitriol yields hydrogen to the chlorine of the common salt, whilst the oxygen combines with the sodium and forms soda, which unites with the sulphuric acid to form sulphate of soda, as is shown in the following diagram:—

Preparation of Hydrochloric Acid Gas.

Before decomposition.		After decomposition.
1 Eq. Chloride of sodium, NaCl.	1 eq. Chlorine 1 eq. Sodium	1 eq. hydrochloric acid gas, HCl.
1 eq. Oil of vitriol, HO, SO_3	1 eq. Oxygen 1 eq. Hydrogen 1 eq. Sulph. acid	1 eq. Sulphate of soda, NaO, SO_3;

or simply thus; $NaCl + HO, SO_3$ yield $HCl + NaO, SO_3$.

Properties.—Hydrochloric acid is a colourless gas, of a peculiar, pungent odour, and an intensely acid taste; it irritates the eyes, and if breathed even when largely diluted produces coughing. It is also very injurious to vegetation, causing the leaves to shrivel and turn brown. It is heavier than air; 100 cubic inches weighing 39·64 grains. Under a pressure of 40 atmospheres at 50° it is condensed to a colourless liquid of sp. gr. 1·27, which dissolves bitumen, and which has never been frozen; the refracting power of this liquid is less than that of water. Hydrochloric acid gas is incombustible, and extinguishes burning bodies. It reddens dry litmus paper; when allowed to escape into the air it produces white fumes by condensing the atmospheric moisture, and forming with it a body less volatile than pure water. It is instantly absorbed by water: a lump of ice liquefies in a jar of the gas and absorbs it in a moment.

(315) *Solution of Hydrochloric Acid.*—The solution of hydrochloric acid in water is an indispensable requisite in the laboratory. It is easily prepared for use by placing in a capacious retort 3 parts of fused chloride of sodium in fragments, and introducing gradually, through a bent funnel, 5 parts of oil of vitriol. If pounded salt be used, the action of the acid is apt to be too rapid. The retort is connected with a series of Woulfe's bottles; in the first a small quantity of water is placed to detain any impurities which might be carried over mechanically with the gas; the second bottle may contain 4 parts of water, and should be immersed in a vessel of cold water, as the condensation of the gas is attended with a great disengagement of heat. On applying a gentle heat to the retort the acid comes over and is condensed; an easily soluble acid sulphate of soda remains in the retort, and is formed as follows:—

$$\overbrace{NaCl}^{\text{Chloride sodium.}} + \overbrace{2(HO, SO_3)}^{\text{Sulph. acid.}} \text{ give } \overbrace{HCl}^{\text{Hydrochlor. acid.}} + \overbrace{NaO, HO, 2SO_3}^{\text{Acid sulph. soda.}}.$$

For manufacturing purposes the decomposition is effected in iron

cylinders, like those employed in the preparation of nitric acid, and only one half the quantity of sulphuric acid prescribed above is used. The acid in this case is in the proportion of one equivalent to each equivalent of salt, neutral sulphate of soda remaining in the cylinder, whilst the acid is condensed in a series of salt-glazed stoneware jars, arranged as Woulfe's bottles (488).

Water at 40° absorbs nearly its own weight, or about 480 times its bulk of hydrochloric acid, increasing in volume about one third, and acquiring a density of 1·2109. It forms a colourless, fuming liquid, which, by a slight elevation of temperature, parts with the gas abundantly; at this strength it contains nearly 43 per cent. of acid, being about in the proportion of 1 equivalent of acid to 6 equivalents of water.

If the strong acid be placed in a retort, and distilled, it loses hydrochloric acid, until the liquid which remains has a density of 1·100 at 60°; at this point it distils unchanged. A weaker acid if distilled parts with its water freely, until it acquires the density of 1·100, and then it likewise distils unchanged, at a temperature of 233°. Such an acid contains about 20 per cent. of hydrochloric acid, and consists of 16 equivalents of water and 1 of hydrochloric acid.* Common hydrochloric acid may therefore easily be purified by dilution till it has a sp. gr. of 1·1 and then distilling.† Bineau, by concentration of the acid at the ordinary temperature of the air *in vacuo* over sulphuric acid, obtained a hydrate ($HCl + 12 Aq$) of sp. gr. 1·128, containing 25 per cent. of the anhydrous acid. According to this observer (*Ann. de Chemie*, III. vii. 259), the vapour of the acid of sp. gr. 1·10 has a density of 0·69, 1 volume of the acid and 8 volumes of aqueous vapour being united without condensation.

The following table indicates the amount by weight hydro-

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* Roscoe and Dittmar (*Q. J. Chem. Soc.*, xii. 128), by varying the pressure under which the distillation is effected, have, however, shown that this apparent constancy of composition is really an accidental circumstance, and that there is no definite hydrate of this acid; but that for every pressure an aqueous solution exists, which, when distilled under that pressure, possesses a fixed composition and fixed boiling point. Thus, when distilled under a pressure of 2 inches of mercury, the distillate contained 23·2 per cent. of hydrochloric acid; distilled under 15 inches, the per-centage of acid was 21·3, corresponding to the formula $HCl+15Aq.$; whilst under a pressure of 30 inches the per-centage of acid was reduced to 20·24 ($HCl+16 Aq$); if distilled under a pressure of 60 inches, the amount of acid fell to 19·0; and under 90 inches as low as 18·2 of HCl per cent.; the composition of the liquid in the last case corresponding nearly to $HCl+18Aq$. Water at 32°, according to these observations, dissolves 0·825 its weight of hydrochloric acid gas, under a pressure of 30 inches of mercury; and at 60° it dissolves 0·745 of its weight.

† Chlorine, however, as well as chloride of arsenic and sulphurous acid, passes over in the distillate, if present.

chloric acid in 100 parts of solution of the acid of the various densities therein enumerated, at a temperature of 77° :—

Strength of Hydrochloric Acid. (*E. Davy.*)

Specific gravity.	Hydrochloric acid in 100 parts.	Specific gravity.	Hydrochloric acid in 100 parts.
1·21	42·43	1·10	20·20
1·20	40·40	1·09	18·18
1·19	38·38	1·08	16·16
1·18	36·36	1·07	14·14
1·17	34·34	1·06	12·12
1·16	32·32	1·05	10·10
1·15	30·30	1·04	8·08
1·14	28·28	1·03	6·06
1·13	26·26	1·02	4·04
1·12	24·24	1·01	2·02
1·11	22·22		

Commercial hydrochloric acid is liable to be contaminated with iron, which gives it a yellow colour; and with the chlorides of sodium and arsenic, the latter derived from the sulphuric acid employed in its preparation. Sulphuric and sulphurous acids, and free chlorine are also often present in it. If pure, the acid should leave no residue when evaporated; on saturating it with ammonia it should give no precipitate of oxide of iron; sulphuretted hydrogen should produce no turbidity in it, which would be the case if arsenic, free chlorine, or sulphurous acid were present; and on dilution with three or four times its bulk of water, no white cloud of sulphate of baryta should be produced by the addition of chloride of barium.

A solution of hydrochloric acid is decomposed by all the metals which decompose water at a red heat: the metal is dissolved, and hydrogen gas is set free, just as when iron or zinc is acted upon by diluted sulphuric acid: for example:—

$$HCl + Zn = ZnCl + H.$$

(316) *Action of Hydrochloric Acid on Metallic Oxides.*—The action of hydrochloric acid upon the oxides of the metals is peculiar. Protoxides are dissolved by the acid, and appear to combine with it; but on evaporating the liquid, a compound is obtained, in which neither hydrochloric acid nor the metallic oxide is present, and which contains neither hydrogen nor oxygen; when soda, for example, combines with hydrochloric acid, the hydrogen of the acid is exactly sufficient by combination with the oxygen of the oxide to form water, which remains in the solution, or else evaporates on the application of heat, whilst the metal and the chlorine

unite directly with each other, as is shown by the following symbols:—

$$\overbrace{NaO, HO}^{\text{Soda.}} + \overbrace{HCl}^{\text{Hydrochlor. acid.}} \text{ yield } \overbrace{NaCl}^{\text{Chloride of sodium.}} + \overbrace{2\,HO.}^{\text{Water.}}$$

But though the metal may exist in solution in the form of chloride, this circumstance does not prevent its precipitation in the form of oxide, when a strong base, such as potash, is added to a solution which contains the chloride of the metal in question, provided that the metal be capable of forming an oxide insoluble in water. For example, if to a solution of chloride of copper a solution of potash be added, the potassium displaces the copper from the chlorine, and the oxygen, with which the potassium was previously combined, is transferred to the copper, whilst the hydrated oxide of copper is precipitated. It is, in fact, an ordinary instance of double decomposition:—

$$\overbrace{CuCl}^{\text{Chloride of copper.}} + \overbrace{KO, HO}^{\text{Potash.}} = \overbrace{KCl}^{\text{Chloride of potassium.}} + \overbrace{CuO, HO.}^{\text{Oxide of copper.}}$$

A reaction not less instructive occurs when oxides containing a larger proportion of oxygen than the protoxides are treated with hydrochloric acid. When, for instance, 1 atom of sesquioxide of iron (Fe_2O_3) is subjected to its influence, 3 atoms of hydrochloric acid are decomposed, 3 atoms of water are formed, and 1 atom of sesquichloride of iron is obtained in solution:—

$$\overbrace{3\,HCl}^{\text{Hydrochlor. acid.}} + \overbrace{Fe_2O_3}^{\text{Sesquiox. of iron.}} \text{ give } \overbrace{3\,HO}^{\text{Water.}} + \overbrace{Fe_2Cl_3.}^{\text{Sesquichlor. of iron.}}$$

It sometimes happens that no chloride corresponding to the oxide exists. There is, for example, no bichloride of manganese: in this case 1 atom of the binoxide of manganese decomposes 2 atoms of hydrochloric acid; 2 atoms of water and 1 atom of protochloride of manganese are formed, whilst the second atom of chlorine is liberated; this being in fact the usual mode of obtaining chlorine gas:—

$$\overbrace{MnO_2}^{\text{Oxide of manganese.}} + \overbrace{2\,HCl}^{\text{Hydrochloric acid.}} \text{ give } \overbrace{MnCl}^{\text{Chloride of manganese.}} + \overbrace{2\,HO}^{\text{Water.}} + \overbrace{Cl.}^{\text{Chlorine.}}$$

The presence of hydrochloric acid and of the soluble chlorides in solution is indicated by the formation of a white, insoluble, curdy precipitate of chloride of silver, when a solution of nitrate of silver is added to the liquid: for example—

$$\underbrace{NaCl}_{\text{Chloride of sodium.}} + \underbrace{AgO, NO_5}_{\text{Nitrate of silver.}} \text{ give } \underbrace{AgCl}_{\text{Chloride of silver.}} + \underbrace{NaO, NO_5}_{\text{Nitrate of soda.}}.$$

This precipitate is soluble in ammonia, but insoluble in nitric acid.

(317) AQUA REGIA: *Nitro-Muriatic Acid.*—The name of aqua regia was given by the alchemists to a mixture of nitric with hydrochloric acid, from the power that it possesses of dissolving gold, the 'king of metals.' Both platinum and gold are insoluble in either acid separately; but when the two acids are mixed, they decompose each other; free chlorine, and abundant ruddy fumes, long mistaken for peroxide of nitrogen, being liberated. The chlorine in the moment of its extrication acts upon the metals and dissolves them. The nature of the reaction and the true composition of these fumes were first correctly ascertained by Gay-Lussac; the investigation formed indeed one of the last scientific labours of this distinguished chemist (*Ann. de Chimie,* III. xxiii. 203).

Chloro-Nitric Gas (NO_2Cl_2); *Boiling Point,* 19°.—If a mixture of 1 part of concentrated nitric acid and 3 parts of hydrochloric acid be placed in a flask and subjected to a gentle heat in the water bath, A, fig. 273, red fumes pass off in abundance. These

FIG. 273.

vapours, if transmitted through a bottle, B, which may be cooled by immersion in melting ice, deposit a little volatilized hydrochloric acid and water, but the red fumes pass on, and may be condensed as a heavy red liquid in the tube receiver, C, which is plunged into a mixture of ice and salt, while free chlorine escapes from the open

extremity of the tube, c, and appears in the bottle, D. The liquid may be preserved by sealing up the fine tubes on either side by means of the blowpipe. The object of drawing out the extremities of the tube, c, is to protect the corks through which they pass from the corrosive action of the chloro-nitrous vapour. If it be desired to collect the compound for analysis, a bent tube filled with chloride of calcium may be interposed between B and c, to absorb all traces of moisture. In this reaction 1 equivalent of nitric acid decomposes 3 equivalents of hydrochloric acid, producing 1 equivalent of the red compound (NO_2Cl_2) (which may be termed *chloro-nitric* gas), 4 equivalents of water, and 1 equivalent of free chlorine:—

$$\overbrace{HO, NO_5}^{\text{Nitric acid.}} + \overbrace{3\,HCl}^{\text{Hydrochlor. acid.}} = \overbrace{NO_2Cl_2}^{\text{Chloro-nitric gas.}} + \overbrace{4\,HO}^{\text{Water.}} + \overbrace{Cl.}^{\text{Chlorine.}}$$

Chloro-nitric gas may be regarded as peroxide of nitrogen in which 2 equivalents of chlorine have taken the place of 2 equivalents of oxygen. At all temperatures above 19° it is a gas of a deep lemon-yellow colour, with the suffocating odour of aqua regia. It may be condensed, by transmitting it through a tube surrounded by a freezing mixture of ice and salt, when it forms a transparent, red, fuming liquid. Water decomposes the compound immediately, appearing to dissolve it: but the solution contains hydrochloric acid and the elements of peroxide of nitrogen:—

$$\overbrace{NO_2Cl_2}^{\text{Chloro-nitric gas.}} + \overbrace{2\,HO}^{\text{Water.}} \text{ give } \overbrace{NO_4}^{\text{Peroxide of nitrogen.}} + \overbrace{2\,HCl.}^{\text{Hydrochlor. acid.}}$$

A similar decomposition ensues when it is mixed with an alkaline base, for it does not form salts. The gas cannot be confined over mercury, since it attacks the metal instantly, forming calomel and liberating deutoxide of nitrogen:—

$$\overbrace{NO_2Cl_2}^{\text{Chloro-nitric gas.}} + \overbrace{4\,Hg}^{\text{Mercury.}} \text{ give } \overbrace{2\,(Hg_2Cl)}^{\text{Calomel.}} + \overbrace{NO_2.}^{\text{Deutoxide of nitrogen.}}$$

Chloro-Nitrous Gas (NO_2Cl).—When chlorine is mixed with deutoxide of nitrogen in the gaseous state, they combine and yield a dense orange-coloured gas; 4 volumes of the deutoxide and 2 of chlorine produce 4 volumes of the new compound. It cannot be formed over mercury, as it is immediately decomposed by this metal. At a temperature of 0° it is reduced to a red liquid resembling the chloro-nitric compound in odour and aspect.

Aqua regia, under certain circumstances, may produce both

chloro-nitric and chloro-nitrous gas, just as the deutoxide of nitrogen may, according to the circumstances under which it is mixed with oxygen, form nitrous acid, or peroxide of nitrogen. In the early stages of the decomposition of aqua regia, the product is nearly pure chloro-nitric gas (NO_2Cl_2), but as the decomposition advances, the quantity of chloro-nitrous gas (NO_2Cl) increases. Neither of these chlorinated compounds exerts any solvent action upon gold or platinum.

Aqua regia is largely employed as an oxidizing agent; by its action perchlorides of the metals are formed in solution, and when the liquid is decomposed by an alkali, the oxide of the metal corresponding in composition to the perchloride is precipitated. By boiling the solutions of the metals in aqua regia with an excess of hydrochloric acid, the whole of the nitric acid may be decomposed and expelled, and a pure solution of the metallic chlorides with excess of hydrochloric acid will be formed.

OXIDES OF CHLORINE.

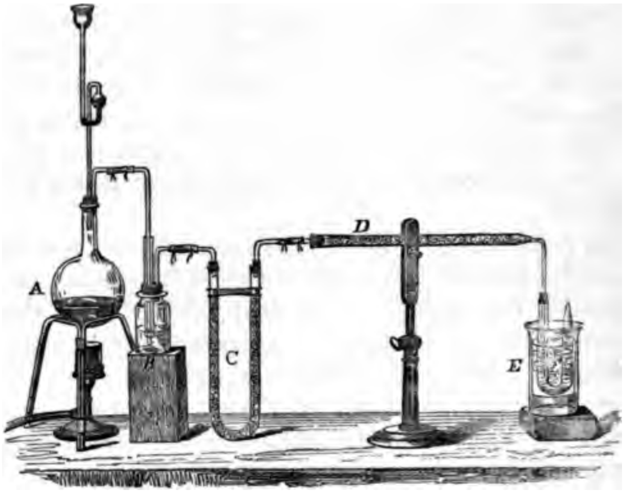
(317*a*) The affinity of chlorine for oxygen is so feeble that the two elements do not enter directly into combination with each other. Several compounds of oxygen and chlorine may however be obtained by indirect methods. Five of these oxides will now be described; they are the following—

		In 100 parts.	
		Chlorine.	Oxygen.
Hypochlorous acid	$ClO = 43.5$	81·60	18·40
Chlorous acid	$ClO_3 = 59.5$	59·66	40·34
Peroxide of chlorine	$ClO_4 = 67.5$	52·59	47·41
Chloric acid	$ClO_5 = 75.5$	47·19	52·81
Perchloric acid	$ClO_7 = 91.5$	38·79	61·21

(318) HYPOCHLOROUS ACID, or *Hypochlorous Anhydride* $(ClO)_2$ or ($ClO=43.5$); *Sp. Gr.* 2·977; *Comb. Vol.* 2; *Boiling Pt.* about 68°. —If chlorine in a perfectly dry state be passed slowly through a tube, D, fig. 274, filled with well dried oxide of mercury obtained by precipitation from a solution of corrosive sublimate by means of potash, immediate action commences; and a gas is produced which may be condensed into a liquid by surrounding the receiver, E, with a mixture of ice and salt. The chlorine is prepared in the flask, A, washed in water in the bottle, B, and dried by allowing it to traverse the bent tube, C, which is filled with pumice-stone moistened with oil of vitriol.

The reaction between the chlorine and oxide of mercury appears to be of a simple nature. An equivalent of chlorine displaces the oxygen from the mercury, and this oxygen at the moment of its

FIG. 274.



liberation unites with a second equivalent of chlorine to form hypochlorous anhydride:—

$$\underbrace{HgO}_{\text{Oxide merc.}} + \underbrace{ClCl}_{\text{Chlorine.}} = \underbrace{HgCl}_{\text{Chlor. merc.}} + \underbrace{ClO.}_{\text{Hypochlor. anhyd.}}$$

Hypochlorous anhydride is thus procured as a deep red liquid, which emits a vapour of a deeper colour than that of chlorine, with a peculiar suffocating chlorous smell. This vapour is remarkable for the ease with which it is decomposed, the warmth of the hand causing its separation into chlorine and oxygen with explosion; 2 volumes of the anhydride in this way produce a mixture composed of 2 volumes of chlorine and 1 volume of oxygen. The composition of the gas is therefore as follows:—

			By weight.		By volume.			Sp. gr.
Chlorine	Cl	=	35·5	or 81·6	2	or 1·0	=	2·453
Oxygen	O	=	8	18·4	1	0·5	=	0·552
Hypochlorous acid	ClO	=	43·5	100·0	2	1·0	=	3·005

Water dissolves about 200 times its bulk of hypochlorous acid gas, and forms with it a pale yellow solution, which has an acrid, but not sour taste. In a concentrated form this solution is very unstable; it acts as a powerful oxidizing agent; but is rapidly decomposed when exposed to the light, bubbles of chlorine escaping from it, whilst chloric acid is formed. Charcoal, iodine, sulphur, selenium, phosphorus, arsenicum, and finely powdered antimony, decompose a solution of hypochlorous acid rapidly, and are converted

by it respectively into carbonic, iodic, sulphuric, selenic, phosphoric, arsenic, and antimonic acids: if the solution be concentrated the action is sometimes attended with explosion. Iron filings are also immediately oxidized with evolution of chlorine. Silver is converted into chloride whilst oxygen is liberated, and copper and mercury combine with both the elements of the acid and are converted into oxychlorides. The contact of chloride of silver with the solution of the acid also decomposes the latter, causing the separation of its constituents in the gaseous form, whilst the metallic chloride appears to have undergone no alteration. Hypochlorous acid attacks the skin and turns it brown; but its most important property is its bleaching power, which, according to the experiments of Gay-Lussac, is twice as great as that of the chlorine which it contains. When hypochlorous acid or any of its salts is heated with hydrochloric acid in excess, an atom of each acid is decomposed, water is formed, and 2 atoms of chlorine are liberated:—

$$HCl + ClO \text{ becoming } HO + ClCl.$$

If a fragment of sal ammoniac be suspended in a solution of hypochlorous acid, oily looking drops of the explosive chloride of nitrogen (325) are formed.

Hypochlorous acid combines with the alkalies and earths, and forms with them salts termed *hypochlorites*. These compounds are decomposed even by feeble acids, such as the carbonic; and the hypochlorous acid thus liberated shows its usual bleaching action on vegetable colours. The solutions of these salts are decomposed by gently heating them, and they become converted into a mixture of chloride and chlorate: thus—

$$3\,(\overbrace{KO,\ ClO}^{\text{Hypochlorite of potash.}}) \text{ become } 2\ \overbrace{KCl}^{\text{Chloride of potassium.}} + \overbrace{KO,\ ClO_5}^{\text{Chlorate of potash.}}.$$

This change is retarded by the addition of an excess of caustic alkali.

When chlorine acts upon bases which have but a feeble affinity for oxygen, these bases are often completely decomposed. In consequence of this reaction, a weak solution of hypochlorous acid is easily prepared by agitating 1 part of the red oxide of mercury with 12 parts of water in a large bottle of chlorine gas, care being taken that the oxide of mercury is in slight excess. The chlorine is rapidly absorbed; part of the oxide of mercury is decomposed by the chlorine, and the chloride of mercury thus produced unites with a portion of unchanged oxide of mercury, forming a brown insoluble oxychloride of that metal; the solution on being decanted

is found to contain hypochlorous acid. The reaction may be represented as follows :—

$$3\,\overbrace{HgO}^{\text{Oxide of mercury.}} + \overbrace{ClCl}^{\text{Chlorine.}} = \overbrace{(2\,HgO,HgCl)}^{\text{Oxychloride of mercury.}} + \overbrace{ClO}^{\text{Hypochlor. acid.}}$$

(319) *Bleaching Compounds.*—If the base upon which chlorine is made to act be a powerful one, like the alkalies or alkaline earths, the gas is absorbed, and peculiar compounds possessed of bleaching properties are produced. It is in this way that the bleaching compounds so extensively used in the arts under the names of chloride of lime, chloride of potash, and chloride of soda, are prepared.

Of these bleaching compounds the chloride of lime is the most important. It is prepared by slaking well-burnt lime, and exposing it to the action of chlorine gas in layers of 2 or 3 inches in thickness, upon perforated shelves in chambers made of lead, or of Yorkshire flagstones. The chlorine must be admitted gradually, in order to prevent too rapid a rise of temperature consequent upon a quick absorption of the gas. If the heat be allowed to rise beyond 100° or 110° F., a quantity of chloride of calcium and of chlorate of lime is formed, the reaction being similar to that which occurs during the preparation of chlorate of potash (321). Slaked lime (CaO, HO) may in this operation be made to take up about half its weight of chlorine; but it is not possible to combine hydrate of lime in the form of powder with an entire equivalent of chlorine so as to form the compound CaOCl: the product always contains a considerable excess of uncombined lime.* Many che-

* A few years ago, Mr. Dunlop, of the St. Rollox Works, Glasgow, introduced a method of preparing chlorine for the manufacture of bleaching powder, by decomposing a mixture of common salt and nitrate of soda with sulphuric acid. In this operation chlorine and nitrous acid are evolved, whilst sulphate of soda is produced; the reaction may be traced by the equations following :—

$$2\,\overbrace{NaCl}^{\text{Chlor. sod.}} + \overbrace{NaO,NO_5}^{\text{Nitrate of soda.}} + 3\,\overbrace{(HO,SO_3)}^{\text{Sulph. acid.}} = 3\,\overbrace{(NaO,SO_3)}^{\text{Sulphate of soda.}} + \overbrace{2\,Cl}^{\text{Chlorine.}} + \overbrace{NO_3}^{\text{Nitrous acid.}} + 3\,HO.$$

The mixed gases are made to pass through a vessel containing oil of vitriol, by which the nitrous acid is rapidly absorbed, whilst the chlorine passes on to the lime. A current of air is made to act on the nitrous sulphuric acid, by which the nitrous acid becomes converted into nitric acid owing to the absorption of oxygen, and the mixed acids being made to act upon fresh chloride of sodium, without the addition of nitre, give rise to a similar succession of decompositions :—

$$2\,\overbrace{(HO,SO_3)}^{\text{Sulph. acid.}} + \overbrace{(HO,NO_5)}^{\text{Nitric acid.}} + 2\,\overbrace{NaCl}^{\text{Chloride of sodium.}} = 2\,\overbrace{(NaO,SO_3)}^{\text{Sulph. soda.}} + \overbrace{2\,Cl}^{\text{Chlorine.}} + \overbrace{NO_3}^{\text{Nitrous acid.}} + 3\,HO.$$

The nitrous sulphuric acid may also be at once made use of in the leaden chambers in the manufacture of oil of vitriol (345).

mists consider both this compound and the corresponding compounds with potash and soda to be hypochlorites of the bases which enter into their formation: in this case they must be double salts of the hypochlorite of the oxide and chloride of the metal. This however is more than questionable: they are probably direct combinations of chlorine with the oxides. If the compound be supposed to be a pure chloride of lime or oxychloride of calcium, the reaction is simply an absorption of chlorine, by which the compound, CaOCl, is formed; but if it be supposed that a hypochlorite is produced, the following decomposition must occur:—

$$\overbrace{2\,(\mathrm{CaO, HO})}^{\text{Hydrate of Lime.}} + \overbrace{\mathrm{ClCl}}^{\text{Chlorine.}} = \overbrace{\mathrm{CaCl}}^{\text{Chloride of calcium.}} + \overbrace{\mathrm{CaO, ClO}}^{\text{Hypochlorite of lime.}} + \overbrace{2\,\mathrm{HO}}^{\text{Water.}}$$

Chloride of calcium is deliquescent, and is soluble in alcohol; but bleaching powder, when properly made, is not deliquescent, and yields scarcely any chloride of calcium to alcohol.

Chloride of lime emits the peculiar odour of hypochlorous acid when exposed to the air; under these circumstances it gradually absorbs carbonic acid and exhales chlorine,—a circumstance which causes it to be frequently used as a disinfecting agent. Cloths dipped in an aqueous solution of the chloride, when hung up in the room to be fumigated, continue for many hours gradually to emit chlorine, but in quantities too small to be injurious to the inmates. Chloride of lime is only partially soluble in water, and leaves a large residue of hydrate of lime. An excess of any acid when poured upon the powder causes a free evolution of chlorine; but if the aqueous solution be mixed with half the quantity of sulphuric acid required to neutralize the lime, hypochlorous acid may be distilled off and condensed in a diluted form in a suitable receiver. The reaction which occurs may be thus represented:—

$$\overbrace{2\,(\mathrm{CaOCl})}^{\text{Chloride of lime.}} + \overbrace{\mathrm{HO, SO_3}}^{\text{Sulph. acid.}} \text{ yield } \overbrace{\mathrm{CaO, SO_3}}^{\text{Sulph. lime.}} + \overbrace{\mathrm{CaCl}}^{\text{Chloride. of calcium.}} + \overbrace{\mathrm{HO, ClO}}^{\text{Hypochlorous acid.}}$$

Chloride of lime is consumed in vast quantities in the bleaching of calicoes and other woven goods. The calico is well washed, and boiled successively with lime water and a weak solution of caustic soda, in order to remove the weaver's dressing, and greasy and resinous matters; it is then digested in a solution of chloride of lime, containing 2 or 2½ per cent. of bleaching powder. The bleaching effect of this solution is not however rendered apparent till the goods are immersed in very dilute sulphuric acid, which decomposes the chloride of lime immediately, and by liberating

chlorine within the fibres of the cloth itself, rapidly removes the colour. Still, however, it is not perfectly white. The calico is therefore washed, and a second time subjected to the action of alkali, to remove the colouring matter now rendered soluble in it by the action of the chlorine; again it is passed through a weaker solution of chloride of lime, and then through dilute acid; finally it is thoroughly washed in a copious stream of water, in order to remove the last traces of sulphuric acid, which would otherwise destroy the fibre.

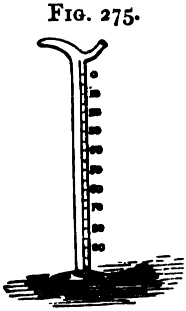
(320) *Estimation of the Bleaching Power of Chloride of Lime.* —The commercial value of bleaching powder depends upon the quantity of chlorine which can be liberated from it by the addition of an acid; for it is this portion of its chlorine only which is available for bleaching purposes. Gay-Lussac proposed to estimate the bleaching power by measurement of the bulk of a solution of indigo of known strength which a given weight of the chloride is able to deprive of its blue colour; and subsequently he determined the amount of available chlorine by the quantity of a standard solution of arsenious acid which could be converted by a known weight of the bleaching powder into arsenic acid.

A still more convenient plan has been described by Graham. It depends upon the determination of the quantity of a protosalt of iron which a given weight of bleaching powder in the presence of an excess of acid can convert into a salt of the sesquioxide of iron: if protosulphate of iron be used, 1 atom of chlorine is required for the conversion of 2 atoms of that salt into 1 atom of sesquisulphate of iron; the chlorine decomposing water and becoming hydrochloric acid, while it liberates a corresponding quantity of oxygen, which combines with the protoxide of iron: thus—

$$2(FeO,SO_3) + 2(HO,SO_3) + CaOCl = Fe_2O_3,3SO_3 + HCl + CaO,SO_3 + HO.$$

Seventy-eight grains of crystallized protosulphate of iron contain a quantity of protoxide which requires 10 grains of chlorine for its conversion into sesquioxide of iron. In making an experiment upon the value of a bleaching powder, 78 grains of clean dry crystals of the protosulphate are dissolved in about 2 ounces of water, and acidulated with sulphuric or hydrochloric acid; 50 grains of the bleaching powder are rubbed up in a mortar with 2 ounces of warm water, and transferred to a burette or tall narrow tube (fig. 275), capable

FIG. 275.



of holding 1000 grains of water, and graduated into 100 equal parts from above downwards. The mortar is washed with a little more water, and the washings added to the liquid in the burette, which is filled up exactly to 0°. The openings at top are closed with the finger and thumb, and the contents of the vessel are mixed thoroughly by agitation. The solution of chloride of lime is then added gradually to the sulphate of iron, (constantly stirring the mixture,) until the whole of the iron is peroxidized. The progress of the oxidation is ascertained by means of a solution of the red prussiate of potash, which strikes a deep blue with the liquid if it contain any unchanged protosulphate. Several drops of this liquid are spotted over a white plate, and after each addition of the chloride of lime to the protosulphate, a drop of the iron solution is mixed with one of these, and the addition of the chloride is continued so long as the blue colour appears. The stronger the bleaching powder, the fewer will be the number of divisions required to be poured from the burette. This number of divisions divided by 2 will indicate the number of grains of bleaching powder which contain 10 grains of available chlorine. The strength of the powder is therefore obtained by the following proportion, in which m represents the number of measures poured from the burette:—

$\frac{m}{2} : 10 :: 100 : x$ (the number of grains of chlorine in 100 grains of the powder); or $\frac{2000}{m} = x$.

The process of converting a protoxide of a metal into one of its higher oxides, by means of chloride of lime, admits of being employed in a variety of other cases, a solution of chloride of lime, when mixed with hydrochloric acid, being in fact a powerful oxidizing agent. Peroxide of bismuth, of cobalt, of nickel, and of lead, may be obtained readily by adding a neutral solution of chloride of lime to neutral solutions of the salts of these metals and heating the liquid.

(321) Chloric Acid, ($HO,ClO_5 = 9 + 75\cdot5$).—This compound is not known in the anhydrous form, and has never been obtained with less than 1 equivalent of water as a hydrate (HO,ClO_5). If a current of chlorine gas be caused to pass through a solution of caustic potash, it is rapidly absorbed, even when transmitted in a continuous stream, and a bleaching liquid is formed, which, on the application of heat, loses its bleaching properties, and is gradually converted into a mixture of chloride of potassium and chlorate of potash; 6 equivalents of chlorine and 6 of potash furnishing 5 of chloride of potassium and 1 equivalent of the chlorate:—

$$6\ Cl+6\ (KO, HO)=5\ KCl+KO, ClO_5+6\ HO.$$

The chlorate of potash being sparingly soluble is freed from the chloride by two or three crystallizations. In order to obtain chloric acid, the salt is decomposed by the addition of hydro-fluosilicic acid, which forms an insoluble compound with the potash, and chloric acid is liberated; the acid solution may be poured off from the precipitate, and concentrated by evaporation over the water-bath at a heat not exceeding 100° F., till it forms a syrupy liquid of a faint chlorous smell, and a powerfully acid taste. It is instantly decomposed by contact with organic matter, and in its concentrated form it chars and even sets fire to paper. By a temperature a little above 100° the acid is decomposed into oxygen gas, chlorine, and perchloric acid, 2 (HO,ClO_5) yielding HO,ClO_7+HO+O_2+Cl. In diffused daylight, it gradually undergoes spontaneous decomposition. On one occasion a small specimen which I had sealed up in a glass tube was placed aside upon a shelf; but in a few weeks, although left untouched, the tube exploded in consequence of the expansive force of the liberated gases.

Chloric acid, when in combination, requires a higher temperature for its decomposition. The action of heat upon chlorate of potash has already been mentioned as affording a very convenient source of pure oxygen (285). This salt, when heated to a point a little short of redness, fuses and is converted into chloride of potassium and oxygen gas; KO, ClO_5 becoming $KCl+O_6$.

This decomposition also furnishes data for ascertaining the composition of chloric acid; for if a given weight of the chlorate be calcined with suitable precaution, the loss indicates the entire quantity of oxygen which it contained, due both to the chloric acid and to the potash. The proportions of chlorine and of potassium in chloride of potassium being known, the composition of chloric acid is readily calculated.

Chlorates.—The salts of chloric acid, or the *chlorates*, are monobasic. All of them are decomposed by heat; oxygen is expelled, and generally a chloride of the metal is left behind; the chloride can be detected in the residue by nitrate of silver. The chlorates produce scintillation when thrown upon ignited charcoal; and when heated with combustible substances, such as phosphorus or sulphur, they explode violently; it generally happens that mere friction with these bodies is sufficient to cause a powerful detonation: for example, if half a grain of sulphur be triturated in a mortar with 2 or 3 grains of chlorate of potash, the friction is attended with a series of small explosions. When a fragment of a chlorate

is placed in a drop of oil of vitriol, a yellow colour is produced, and the peculiar odour of peroxide of chlorine is evolved. Many of the chlorates are deliquescent; they are all soluble in water; the salt formed with the suboxide of mercury is least so; their solutions are not precipitated by nitrate of silver; many of them also are soluble in alcohol. Paper soaked in a solution of a chlorate, and allowed to dry, acquires the property of smouldering when kindled, and burns in the same manner as touch-paper. The chlorates when in solution, even in small quantity, may readily be distinguished from the nitrates, by adding first a few drops of a solution of indigo, and then a solution of sulphurous acid: the blue colour immediately disappears even without the application of heat, but it remains unaltered when nitrates only are present. The chlorates of potash, soda, and silver are anhydrous, that of baryta contains 1 atom of water, and that of strontia 6 atoms of wafer.

Chlorate of potash, when in solution, often affords a convenient method of converting the metallic protoxides into peroxides; since by the addition of hydrochloric acid to the solution, chloric acid is set at liberty, and exerts its oxidizing power. Iron, for example, when it exists in a solution as a protosalt, is thus readily converted into a persalt when the liquid is boiled.

(322) Perchloric Acid, ($HO, ClO_7 = 9 + 91{\cdot}5$).—If instead of heating the chlorate of potash to complete decomposition, the temperature be moderated and the process stopped when one third of the total quantity of oxygen has been expelled, the mass will have assumed a pasty condition, and will be found to contain a compound of chlorine with a still higher proportion of oxygen, to which the name of perchloric acid has been given; this compound remains in combination with the potash. The reaction appears to consist in the resolution of 2 atoms of the chlorate into 1 atom of perchlorate (KO,ClO_7) and 1 of chlorite of potash (KO,ClO_3), this latter salt being unable to exist at so high a temperature, is immediately converted into oxygen gas, and chloride of potassium, as follows:—

$$\overbrace{2\,(KO, ClO_5)}^{\text{Chlorate of potash.}} = \overbrace{KO, ClO_3}^{\text{Chlorite of potash.}} + \overbrace{KO, ClO_7}^{\text{Perchlorate of potash.}};\ \text{and}\ \overbrace{KO, ClO_3}^{\text{Chlorite of potash.}} = \overbrace{KCl}^{\text{Chloride of potassium.}} + \overbrace{O_4}^{\text{Oxygen.}}.$$

By crystallization the perchlorate of potash is readily separated from the more soluble chloride. The perchlorate is freely dissolved by boiling water, but as the salt is much less soluble at ordinary temperatures, it crystallizes from the solution as it cools, and is deposited in octohedra. At a red heat the perchlorate is itself resolved into oxygen and chloride of potassium. One method of

obtaining perchloric acid in the form of hydrate consists in distilling the perchlorate of potash with twice its weight of sulphuric acid diluted previously with one tenth of its weight of water: if the receiver be kept cool by ice, the first portions that distil over crystallize; a large proportion of the acid, however, is decomposed into chlorine and oxygen gases. The crystals of the acid are very deliquescent; a saturated solution may be obtained of specific gravity of 1·65, which may be distilled in great part unaltered at a temperature of 392°. This solution is of a purely sour taste, and does not destroy vegetable colours; perchloric acid, indeed, is the most stable of all the oxides of chlorine. It will even dissolve iron and zinc with evolution of hydrogen gas.

Perchloric acid forms the salts known as *perchlorates:* they all contain 1 atom of base to 1 of acid; and in general are deliquescent. None of them are insoluble, though the perchlorate of potash requires upwards of 150 times its weight of cold water for solution: the salts of this acid with soda, baryta, and silver, are soluble in alcohol. All the perchlorates are decomposed by heat, with evolution of oxygen and formation of a chloride, but they may be distinguished from the chlorates by not yielding a yellow gas when moistened with oil of vitriol.

(323) CHLOROUS ACID; *Chlorous Anhydride* $(ClO_3)_2$ or $(ClO_3=59{\cdot}5)$; *Sp. Gr.* 2·646, *Comb. Vol.* 2.—This substance may be obtained in the form of a gas of a deep yellowish-green colour; it is not liquefied by exposure to a temperature of —4° F. Chlorous anhydride is a dangerous compound to prepare, as exposure to a temperature not much exceeding 130° F. is sufficient to decompose it with a powerful explosion. Contact with most combustible nonmetallic elements, such as sulphur, selenium, tellurium, and phosphorus, decomposes the gas with explosion; arsenic has a similar effect. Most of the metals—including copper, lead, tin, zinc, and iron—are without action upon it, but mercury absorbs it completely. A solution of the acid, however, oxidizes all these metals, and they commonly yield a mixture of chlorate and chloride, especially if the acid be in excess; thus, $2\ Zn+2\ ClO_3=ZnCl+ZnO,\ ClO_5$.

The composition of chlorous acid gas is the following:—

			By weight.		Millon.	By vol.		Sp. gr.
Chlorine	Cl	=	35·5	or 59·66	60·15	2	or 0·66	1·635
Oxygen	O_3	=	24·0	40·34	39·85	3	1·00	1·105
Chlorous acid	ClO_3	=	59·5	100·00	100·00	3	1·00	2·740

This gas is soluble in about one sixth of its bulk of water, and the solution, even when diluted very largely, has a bright yellow colour.

The compound is prepared by deoxidizing chloric acid; this object is effected by means of arsenious acid, when the gas is required in a state of purity. Three parts of arsenious acid and 4 of chlorate of potash are rubbed up into a paste with water, and 16 parts of pure nitric acid, of sp. gr. 1·24, are added; the whole is placed in a small flask, which is filled up to the neck with the mixture, and a very gentle heat is applied by means of a water-bath (Millon, *Ann. de Chimie*, III. vii. 322). The gas must be collected by displacement in dry bottles, as it is rapidly decomposed by mercury. In this operation, the arsenious acid becomes oxidized at the expense of the nitric acid; nitrous acid is formed, and this in turn is reconverted into nitric acid by decomposing the liberated chloric acid: for example—

$$\overbrace{AsO_3}^{\text{Arsenious acid.}} + \overbrace{HO, NO_5}^{\text{Nitric acid.}} = \overbrace{AsO_5}^{\text{Arsenic acid.}} + \overbrace{HO, NO_3}^{\text{Nitrous acid.}}\text{; and}$$

$$\overbrace{HO, NO_3}^{\text{Nitrous acid.}} + \overbrace{KO, ClO_5}^{\text{Chlorate of potash.}} = \overbrace{KO, NO_5}^{\text{Nitrate of potash.}} + \overbrace{ClO_3}^{\text{Chlorous anhydride.}} + HO.$$

Chlorous acid possesses considerable bleaching power; it combines slowly with bases, and forms definite salts, termed *chlorites*: they contain 1 atom of acid to 1 of base, like chlorite of potash (KO, ClO_3), which is deliquescent: if its solution be slowly evaporated to dryness, it is converted into a mixture of chloride and chlorate of the base, in equivalent proportions. The chlorites of soda, baryta, and strontia, are also deliquescent. The chlorites are decomposed by the feeblest acids, such even as carbonic acid. Nitrate of lead produces a sulphur-yellow scaly precipitate in their solutions, owing to the formation of a chlorite of lead (PbO, ClO_3). Chlorite of silver is also yellowish and insoluble.

The chlorites may be distinguished from the hypochlorites by the addition of a mixture of arsenious acid in nitric acid, which does not destroy the bleaching power of the chlorites, whilst it destroys that of the hypochlorites. Their solutions deoxidize an acidulated solution of permanganate of potash.

(324) PEROXIDE OF CHLORINE ($ClO_4 = 67{\cdot}5$); *Calcd. Sp. Gr.* 2·33; *Boiling Pt.* 68°.—This compound is gaseous at ordinary temperatures, but by slight pressure, or by exposure to a cold of —4° F., it is reducible to a red liquid. The gas is of a colour still deeper than that of chlorous acid, and has a similar but less irritating odour. Water dissolves about 20 times its bulk of the gas, and forms a yellow solution, which bleaches powerfully. The gas requires great care in its preparation, as a temperature of 140°

or 145° determines its explosion, 4 volumes of this gas furnishing a mixture of 4 volumes of oxygen and 2 of chlorine, its composition being thus represented:—

			By weight.		By vol.		Sp. gr.
Chlorine	Cl	=	35·5 or	52·59	2 or	0·5 =	1·226
Oxygen	O_4	=	32·0	47·41	4	1·0 =	1·105
Peroxide of chlorine	ClO_4	=	67·5	100·00	4	1·0	2·331

Peroxide of chlorine may be thus obtained:—Fused chlorate of potash is broken into coarse fragments, and treated with two thirds of its weight of oil of vitriol, the action being favoured by a very gentle heat. The reaction is rather complicated; 4 atoms of sulphuric acid decompose 3 of the chlorate, 2 atoms of the peroxide of chlorine escape, whilst 2 atoms of acid sulphate of potash and 1 atom of perchlorate are formed:—

$$\overbrace{3\,(KO,\ ClO_5)}^{\text{Chlorate of potash.}} + \overbrace{4\,(HO,\ SO_3)}^{\text{Sulphuric acid.}} =$$

$$2\,\overbrace{ClO_4}^{\text{Perox. chlorine.}} + \overbrace{KO,\ ClO_7}^{\text{Perchlorate of potash.}} + 2\,\overbrace{(KO,\ HO,\ 2\,SO_3)}^{\text{Acid sulphate of potash.}} + 2\,\overbrace{HO.}^{\text{Water.}}$$

Peroxide of chlorine acts rapidly upon mercury, and must therefore be collected by displacement. Mere contact with many combustible matters at once determines its explosion. Place, for instance, 4 or 5 grains of chlorate of potash at the bottom of a tall glass, and pour upon it a little water; then having placed the glass in a deep plate (fig. 276), add a piece of phosphorus of about the size of a pea, and by means of a long funnel pour slowly in about a tea-spoonful of oil of vitriol; flashes of a beautiful green light, attended with a crackling noise, will be immediately produced. If loaf sugar and chlorate of potash be separately powdered, and mixed in equal proportions with each other on a sheet of paper, by means of a spatula, the addition of a drop of sulphuric acid will liberate peroxide of chlorine, which will be decomposed by the combustible matter, and sufficient heat will be emitted to cause the mass to burst into flame, and to deflagrate with great brilliancy. Peroxide of chlorine is not possessed of acid properties; alkaline solutions, however, absorb it rapidly, but when evaporated, they yield a mixture of chlorite and chlorate of the base:—

Fig. 276.

$$\underbrace{2\,ClO_4}_{\text{Perox. chlorine.}} + \underbrace{2\,(KO,\,HO)}_{\text{Potash.}} = \underbrace{KO,\,ClO_3}_{\text{Chlorite of potash.}} + \underbrace{KO,ClO_5}_{\text{Chlorate potash.}} + \underbrace{2\,HO}_{\text{Water.}}.$$

Other oxides of chlorine have been obtained; they have a composition which may be explained by considering them as compounds of chlorous acid with chloric or with perchloric acid; they however present but few points of interest. Davy's *euchlorine*, which is evolved on gently heating a chlorate with hydrochloric acid, is a yellow explosive gas, consisting of a mixture of chlorine with one of these compound oxides, the *chloro-chloric acid* ($2\,ClO_5,ClO_3$) (Millon).

(325) Chloride of Nitrogen (HCl_2N,Cl_3N?), *Sp. Gr. of Liquid*, 1·653.—The affinity existing between chlorine and nitrogen is very feeble; the compound known by the name of chloride of nitrogen is always obtained by indirect means.

If a current of ammoniacal gas be directed into a bottle of gaseous chlorine it will take fire spontaneously, burning with a green flame, whilst hydrochloric acid is formed, and nitrogen is set free; dense white fumes being generated by the union of the hydrochloric acid with undecomposed ammonia. By modifying the experiment, the reaction may be employed as a means of obtaining nitrogen gas, for when a stream of chlorine gas is transmitted through a solution of ammonia, the hydrochloric acid as fast as it is formed combines with undecomposed ammonia, and pure nitrogen is liberated: if the solution be concentrated, each bubble of chlorine produces a flash of light. One atom of ammonia, when decomposed by 3 atoms of chlorine, yields 1 atom of nitrogen; H_3N+3Cl becoming $3HCl+N$.

But if instead of acting on a solution of free ammonia, a bottle of chlorine perfectly clear from greasy matter be inverted over a leaden dish containing a solution of 1 part of sal ammoniac (H_4NCl), in 12 parts of water, drops of a yellow oily-looking liquid gradually collect on the surface of the liquid and fall to the bottom, whilst the chlorine slowly disappears: this liquid is the substance known as *chloride of nitrogen*. A safer method of obtaining this body consists in suspending a fragment of sal ammoniac (say 20 or 30 grains) in a solution of hypochlorous acid; oily drops of the so-called chloride of nitrogen are gradually formed, and sink in the liquid as the salt is dissolved. The new body remains liquid at —16°, but is very volatile, and possesses a peculiar penetrating odour. It is one of the most dangerous compounds known, for it explodes with tremendous violence when heated to between 200° and 212° F., emitting a flash of light

when the detonation occurs. The explosion is so sudden that it invariably breaks any glass or porcelain vessel in which it may be contained: hence a leaden saucer is used in preparing the compound. Chloride of nitrogen also explodes violently at ordinary temperatures when brought into contact with many inflammable substances, such as oil of turpentine, phosphorus, and the fixed oils. The alkalies likewise cause its immediate explosion. On the other hand, it does not explode when touched with the resins, the strong acids, with metallic bodies in general, or with sugar.

Little or nothing is known of the cause of these remarkable reactions, or of the light and heat emitted when the chloride explodes by slightly elevating its temperature; in this case and in the analogous instances of the explosion of the oxides of chlorine, light is emitted, not during the act of combination as is usual, but during the expansion and sudden separation of the two gaseous elements.

The analysis of this body is attended with great difficulty; indeed, considerable doubt exists as to its true composition. It is highly probable that it is not simply a chloride of nitrogen, but a combination of chlorine, nitrogen, and hydrogen (HCl_2N, Cl_3N), somewhat analogous to the corresponding explosive compound which may be formed with iodine (336).

(326) Chlorides of Carbon.—Chlorine does not unite directly with carbon, but Faraday succeeded in procuring several compounds between these elements by the decomposition of Dutch liquid, a combination of carbon and hydrogen with chlorine, obtained under circumstances which will be explained when treating of olefiant gas (400).

Subchloride of Carbon (C_4Cl_2) forms fine, silky crystals, which may be sublimed in closed vessels without change; it is soluble in ether. This substance is obtained by decomposing the protochloride of carbon (C_4Cl_4), by causing it to pass several times through a tube heated to bright redness. If heated in air on platinum foil it burns with a red smoky flame.

Protochloride of Carbon (C_4Cl_4); *Sp. Gr. of Liquid*, 1·552; *of Vapour*, 5·82; *Comb. Vol.* 4; *Boiling Pt.* 248°.—This compound was procured by Faraday from the sesquichloride (C_4Cl_6) by subliming it repeatedly through a tube filled with fragments of glass, heated to redness. It is a transparent, colourless liquid, with an aromatic odour.

Sesquichloride of Carbon (C_4Cl_6); *Sp. Gr. of Solid*, 2·0; *of Vapour*, 8·157; *Comb. Vol.* 4; *Melting Pt.* 320°; *Boiling Pt.* 360°.

—This chloride was originally procured by the action of chlorine upon Dutch liquid (400) (Faraday); but it has since been obtained by the action of chlorine upon a variety of derivatives from the alcohol series (1014 *et seq.*) It is a volatile crystalline solid, with an aromatic odour resembling that of camphor. It is soluble in alcohol, in ether, and in the fixed and volatile oils. An isomeric (413) liquid chloride, the vapour of which has a density of 4·082, and a composition C_2Cl_3, was obtained by Regnault by passing the vapour of bichloride of carbon (C_2Cl_4) through a tube heated to low redness.

Bichloride of Carbon (C_2Cl_4), *Sp. Gr. of Liquid,* 1·599; *of Vapour,* 5·30; *Comb. Vol.* 4; *Boiling Pt.* 172°.—This substance was obtained by Regnault from wood-spirit, from chloroform, and from other derivatives from wood-spirit, by exposing them in the sun to the action of an excess of chlorine. Kolbe also found that a mixture of the vapour of bisulphide of carbon and chlorine, when passed through a porcelain tube heated to redness, yielded the same compound. It is a colourless liquid, which is insoluble in water, but soluble in alcohol and in ether. It becomes a crystalline solid of pearly lustre at —9° F.

(327) Oxychloride of Carbon: *Chlorocarbonic Acid; Phosgene Gas* [$(COCl)_2=99$]; *Sp. Gr.* 3·68; *Comb. Vol.* 4.—When equal measures of carbonic oxide and chlorine are exposed to the direct rays of the sun, they combine, and become condensed into half their volume. The combination takes place slowly in the diffused light of day; but no action occurs if the two gases are mixed together and kept in a dark room. There are other modes of obtaining this compound indirectly; thus it may be prepared by transmitting carbonic oxide gas through heated perchloride of antimony; the action of light is not necessary in this case. This reaction may sometimes be usefully employed as a test for carbonic oxide when mixed in small quantity with other gases, the pungent odour of the oxychloride which is formed being very characteristic. The composition of the gas is the following:—

		By weight.			By volume.		Sp. gr.
Carbonic oxide $(CO)_2$	=	28	or 28·28	4	or	1·0 =	0·967
Chlorine Cl_2	=	71	71·72	4		1·0 =	2·453
Phosgene gas $(CO)_2Cl_2$	=	99	100·00	4		1·0 =	3·420

Oxychloride of carbon is a colourless, suffocating gas, which is immediately decomposed by water into carbonic and hydrochloric acids $(COCl)_2 + 2\,HO = 2\,CO_2 + 2\,HCl$. It does not possess the characters of an acid; but if the gas be mixed

with ammonia in the proportion of 1 volume of phosgene to 4 volumes of ammonia, both gases are condensed, and form a white volatile solid, which is neutral to test paper, destitute of smell, and soluble in water and in alcohol slightly diluted, but insoluble in ether. This compound is regarded by Regnault as a mixture of chloride of ammonium and carbamide:—*

$$4\,H_3N + (COCl)_2 = 2\,H_4NCl + H_4N_2C_2O_2.$$

§ II. Bromine (Br=80).

Comb. Vol. of Vapour, 2; *Sp. Gr. of Vapour,* 5·393; *of Liquid at* 32_o, 3·187; *Melting Pt.* 9·5°; *Boiling Pt.* 145°·4.

(328) Bromine, so named owing to its irritating odour (from βρώμος, 'a stench'), was discovered by Balard in the year 1826, in *bittern,* which is the mother-liquor of sea water after the less soluble salts have been extracted by crystallization. Bromine exists in sea water in minute quantity, varying from one-third of a grain to about one grain in each gallon: it appears to be combined with magnesium, as bromide of magnesium. Many saline springs, such as those of Kreuznach and Kissingen likewise contain bromine in quantity sufficient to render its extraction from them a source of profit. Indeed, few deposits of chloride of sodium exist in which traces of bromine have not been discovered. It has also been found in a silver ore from Mexico, and it is abundant in the mines of Chañarcillo, in South America; in both cases the bromide of silver is mixed with chloride of silver.

Preparation.—In order to obtain bromine, the mother-liquor from the brine, after all the salts separable by crystallization have been removed, is subjected to a current of chlorine, taking care to avoid an excess of this gas, which would occasion inconvenience by forming a compound with the liberated bromine. All the bromides are decomposed readily by chlorine, the affinities of chlorine being more powerful than those of bromine. In the foregoing operation chloride of magnesium is formed, and bromine is set free:—

$$MgBr + Cl = MgCl + Br;$$

the bromine shows itself by giving to the liquid a beautiful and characteristic yellow colour. This yellow liquid, if agitated with ether, parts with its bromine to the ether, which, on standing,

* Natanson considers that the carbamide thus obtained is identical with urea, and not merely isomeric with it as formerly supposed (1367).

rises to the surface, where it forms a beautiful golden yellow layer. The ethereal solution is decanted and agitated with a solution of potash; the yellow colour immediately disappears; bromide of potassium and bromate of potash are formed and dissolved in the water,

$$6\ Br + 6\ (KO,HO) = KO,BrO_5 + KBr + 6\ HO;$$

whilst the ether, after repose, rises again to the surface despoiled of its bromine, and may again be employed in a repetition of the process upon a fresh quantity of bittern. When the solution of potash has, by repeated charges of bromine, been nearly neutralized, the liquid is evaporated to dryness; the saline mass is gently ignited to decompose the bromate, after which it is mixed with peroxide of manganese and distilled in a retort with sulphuric acid: dense red vapours of bromine pass over, which may be collected in a receiver containing water, and kept cool by ice. The decomposition is of the same nature as that attending the liberation of chlorine from sea-salt by means of oxide of manganese and sulphuric acid:—

$$KBr + MnO_2 + 2\ (HO,SO_3) = KO,SO_3 + MnO,SO_3 + 2\ HO + Br.$$

In this operation a small quantity of chlorine passes over with the bromine, since from the manner in which the bromide of potassium is formed, it is always contaminated with a portion of chloride of potassium. The chlorine unites with part of the bromine, forming chloride of bromine, which is partially decomposed and dissolved by the water in the receiver, while the bromine is condensed in red drops. In order to obtain bromine free from chlorine it must be saturated with hydrate of baryta, which produces a mixture of bromide and chloride of barium with bromate of baryta: this mixture must be heated to redness in order to convert the bromate into bromide of barium, and the residue digested in alcohol, which dissolves nothing but the bromide. The bromide of barium is obtained by evaporation of its alcoholic solution, and when heated with black oxide of manganese and sulphuric acid it yields pure bromine.

Properties.—Bromine forms a red liquid, so deep in colour as to be nearly opaque. It has a sp. gr. of 2·966 at 60°: it is very volatile, and emits dense red vapours resembling peroxide of nitrogen in colour. In smell it resembles chlorine, and is extremely irritating to the nose and fauces when respired, even if largely diluted with air. When swallowed it operates as a powerfully irritating poison; it acts rapidly on all the organic tissues, and renders the skin permanently yellow. Bromine boils at

145°·4F. (Pierre), and when exposed to a temperature of 9°·5 it forms a red crystalline solid. The properties of bromine greatly resemble those of chlorine, though they are less strongly developed. It bleaches many vegetable colours. Its vapour will not support the flame of a burning taper. Bromine is slightly soluble in water, and gives to it a yellow colour; it also forms with it a hydrate ($Br + 10HO$; Löwig), which crystallizes in octohedra at 32°. Alcohol dissolves bromine freely, and ether does so still more abundantly. Bromine combines directly with many of the metals, forming compounds termed *bromides* (446), the act of combination being often attended with ignition; even gold combines with it slowly; its compound with silver furnishes a material of considerable value in photographic operations.

(329) Hydrobromic Acid ($HBr=81$); *Sp. Gr.* 2·731; *Comb. Vol.* 4.—Bromine resembles chlorine in its power of combining with hydrogen, and forming with it a very powerful acid, which is a gaseous body consisting of equal measures of hydrogen and bromine vapour united without change of bulk. The mixture of bromine vapour and hydrogen cannot be detonated by the approach of flame, or by the electric spark, but the two elements may be made to unite slowly, by suspending a red-hot platinum wire in the mixture. If moisture be present the occurrence of combination instantly shows itself by the formation of white fumes, which arise from the union of the newly produced gaseous acid with the aqueous vapour.

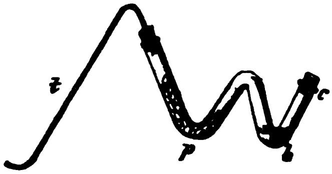
Preparation.—1. Hydrobromic acid gas may be procured abundantly by decomposing bromide of potassium with a concentrated solution of phosphoric acid. If sulphuric acid be used for the purpose, the product is impure, since this acid itself undergoes partial deoxidation.

2.—It may also be obtained by decomposing bromide of phosphorus by means of a small quantity of water, when the following reaction occurs:—

$$PBr_3 + 6\ HO = 3\ HBr + 3\ HO, PO_3;$$

phosphorous and hydrobromic acids being produced. This experiment may be easily performed with the aid of a tube bent as in fig. 277. In the bend *p*, a few fragments of phosphorus and moistened glass are placed, bromine is poured into *b*, and the tube is closed by a cork *c*; on applying a gentle

Fig. 277.



heat at *b*, the bromine is distilled over and comes into contact with the phosphorus; the bromide of phosphorus is decomposed by the water at the moment of its formation, and escapes by the bent tube *t*.

3.—It may also be obtained, but less advantageously, by heating 3 parts of bromine and 6 of crystallized sulphite of soda with 1 part of water, when the sulphite is oxidized at the expense of the oxygen of the water, as follows:—

$$NaO,SO_2 + HO + Br = NaO,SO_3 + HBr.$$

Hydrobromic acid gas is colourless, it is not inflammable, it extinguishes flame, and possesses the usual irritating action of acid gases on the lungs. Faraday succeeded in liquefying the gas under strong pressure; and in a bath of solid carbonic acid and ether, he even obtained it in the form of a solid, which melted at —124°. The acid has the following composition:—

			By weight.		By volume.		Sp. gr.
Bromine ...	Br	= 80	or 98·76	2	or 0·5	=	2·764
Hydrogen ...	H	= 1	1·24	2	0·5	=	0·034
Hydrobromic acid	HBr	= 81	100·00	4	1·0	=	2·798

Hydrobromic acid gas is very soluble in water, forming, when concentrated, a fuming solution of greater density than hydrochloric acid. A solution of the acid of sp. gr. 1·486 (HBr, 10 HO) contains about 47 per cent. of the anhydrous acid; it boils at 259°, and may be distilled without change. (See *note* p. 140.) Chlorine decomposes it immediately; bromine being set free and hydrochloric acid produced.

The action of hydrobromic acid upon the metallic oxides is analogous to that of hydrochloric acid upon them; bromide of the metal and water being produced; thus hydrobromic acid and potash combine, and form bromide of potassium and water; $KO,HO + HBr$ yielding $KBr + 2\ HO$.

Bromides.—The bromides are all solid at ordinary temperatures; most of them are fused by a moderate heat, and are partially volatilized; and the bromides of gold and platinum are decomposed. Most of the bromides are readily soluble in water. They are all decomposed by chlorine, and when in solution they may be recognised by the yellow colour of bromine which is produced by the addition of a few drops of chlorine water. On agitating this yellow solution with ether, the bromine is dissolved by the ether, which on standing separates as a yellow liquid, at the top of the colourless aqueous portion. The bromides, when heated with black oxide of manganese and oil of vitriol, yield red vapours

of bromine: strong nitric acid has a similar effect. Nitrate of silver and nitrate of lead each give a white precipitate with solutions of the bromides, forming bromide of silver ($AgBr$), or bromide of lead ($PbBr$); the bromide of silver is insoluble in cold nitric acid, but is dissolved by large excess of ammonia; but the bromide of lead is dissolved by the addition of diluted nitric acid. Subnitrate of mercury also gives a white precipitate of dibromide of mercury (Hg_2Br) when added to solutions of the bromides: it is soluble in chlorine water with liberation of bromine.

Bromine often combines with the same metal in more than one proportion, and the compounds of bromine correspond almost always, both in number and composition, with those of chlorine with the same metal. Oxybromides may be formed resembling the oxychlorides; and the bromides of the alkaline metals form double bromides with the bromides of the metals which yield acids with oxygen.

(330) Bromic Acid ($HO, BrO_5 = 9 + 120$).—Only one compound of bromine with oxygen is known; and this has never been obtained free from water; it forms an acid corresponding to chloric acid in composition. Bromate of potash is procured by acting on bromine with caustic potash, and from this salt the acid is obtained by a process similar to that employed in the preparation of chloric acid (321). By the action of heat, bromate of potash is decomposed, bromide of potassium being formed, whilst oxygen is liberated. Any solid bromate, when mixed with concentrated sulphuric acid and heated, gives off red fumes of free bromine, while oxygen is evolved. The bromates of silver and suboxide of mercury are anhydrous and sparingly soluble: bromate of lead retains 1 atom of water; it likewise is but slightly soluble. When heated with hydrochloric acid these precipitates evolve free bromine. All the salts of bromic acid which have as yet been prepared are monobasic.

Chloride of Bromine is easily obtained by transmitting chlorine gas through liquid bromine: it is a volatile, reddish-yellow liquid, with a very pungent, irritating odour. Water dissolves it, forming a deep yellow solution possessed of considerable bleaching power.

Bromide of Nitrogen may be obtained by digesting bromide of potassium with the so-called chloride of nitrogen; it forms a detonating oily-looking liquid, resembling chloride of nitrogen in appearance and properties.

§ III. Iodine ($I=127$).

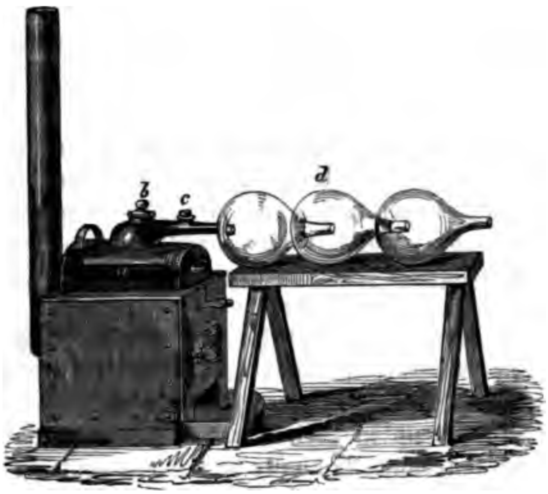
Comb. Vol. 2; *Calculated Sp. Gr. of Vapour*, 8·756; *Observed Sp. Gr.* 8·716; *Sp. Gr. of Solid*, 4·947; *Melting Pt.* 225°; *Boiling Pt.* 347°.

(331) Iodine, the third element in the group which we are now examining, is still denser than bromine, as it assumes the solid form at the ordinary temperature of the air. Its discovery dates back to the year 1811, when it was found by Courtois accidentally in the waste liquors produced in the manufacture of carbonate of soda from the ashes of sea-weed.

Iodine exists in the ocean in quantities still smaller than bromine. It is, notwithstanding, obtained with less difficulty, since the fuci, algæ, sponges, and other marine plants, extract it from sea water, and store it up in their tissues. These, when burnt, give an ash which is technically known as *kelp*; it contains iodine in the form of iodide of sodium. In the mineral kingdom, iodine has been found in one or two rare ores; thus it occurs combined with silver in Mexico, and with zinc in Silesia.

Preparation.—Iodine is at present largely manufactured at Glasgow, from kelp made on the coasts of Scotland and Ireland; the following is an outline of the process adopted in procuring it (Graham):—The sea-weed having been dried in the sun, is burned in shallow excavations, at a low heat; owing to the volatility of the iodide of sodium at a red heat, the loss of this salt would be considerable if the temperature were allowed to rise too high. The half fused ash, or kelp, which remains, is broken into fragments and treated with boiling water, which dissolves about one-half of the ash. The liquid thus obtained is then evaporated in open pans, and all that can be separated by crystallization is removed; a double sulphate of potash and soda, carbonate of soda, and chloride of potassium are thus extracted. The iodine remains in the mother-liquor, which still retains sulphide of sodium, besides hyposulphite, and some carbonate of soda. This liquor, or *iodine ley*, is now mixed with one-eighth of its bulk of oil of vitriol, and allowed to stand for twenty-four hours; carbonic acid, sulphurous acid, and sulphuretted hydrogen gases escape, and sulphate of soda crystallizes out, mixed with a considerable quantity of deposited sulphur. The supernatant liquid is next transferred to a leaden retort of cylindrical form, *a*, fig. 278, supported in a sand-bath, and gently heated from beneath by a small fire; the head of the retort, *b c*, is luted on with clay, and the contents of the retort having been heated to about 140°, a quantity of powdered black

FIG. 278.



oxide of manganese is introduced through the tubulure, *b*. The process must be conducted slowly, at a low temperature; iodine distils over and is condensed in the globular receivers, *d*. It is purified by a second sublimation. The object of the second tubulure, shown at *c*, is to facilitate the clearing of the neck of the retort in case it should become obstructed by the formation of crystals. If the temperature be allowed to rise as high as 212°, the chloride of sodium retained in the ley is decomposed, chlorine is disengaged, and combines with part of the iodine, forming chloride of iodine, which is wasted.

In the foregoing process, the addition of the sulphuric acid occasions the decomposition of the carbonate and hyposulphite of soda, which still remain in solution, as well as of any sulphide of sodium that may be present, forming sulphate of soda which is removed by crystallization. The liquid retains an excess of sulphuric acid, and all the iodide of sodium. When this mixture is heated with peroxide of manganese, the iodine is liberated, whilst sulphate of soda and sulphate of manganese remain in the retort. The process resembles that for bromine:—

$$NaI + MnO_2 + 2\ (HO,SO_3) = NaO,SO_3 + MnO,SO_3 + 2\ HO + I.$$

Properties.—The crystalline form of iodine is an octohedron with a rhombic base; but it is generally obtained in bluish black scales, resembling plumbago in lustre. It is a non-conductor of electricity. At ordinary temperatures, and especially when in a moist condition, it is sensibly volatile, emitting an odour like that of chlorine, but much weaker: when heated it undergoes fusion at 225°; and at about 347° it boils and is converted into a magnificent purple vapour, whence it derives its name (from ἰώδης, 'violet-coloured'). Iodine, when taken internally, acts in large doses as

an irritant poison; but in small quantities it is a most valuable medicine, particularly in glandular swellings, and in certain forms of goître. It stains the skin and most organized substances of a brown colour, and gradually corrodes them. Water forms with it a yellow solution, but dissolves it only in very small quantity. Its bleaching properties are very feeble. Alcohol, ether, hydriodic acid, and solutions of the iodides, dissolve it freely. *Lugol's Solution*, which was formerly much used in medicine, consists of 20 grains of iodine and 30 of iodide of potassium, dissolved in an ounce of water; it is of a deep brown colour. Iodine is also soluble in bisulphide of carbon, to which a minute quantity of iodine imparts a characteristic rich violet colour. Chloroform and benzol likewise dissolve it, forming red solutions. Iodine attacks the metals rapidly, forming compounds termed *iodides;* iron or zinc is readily dissolved by it if placed with it in water, an iodide of the metal being formed. The compounds of iodine with the metals and with hydrogen are decomposed by chlorine, and even by bromine, while the iodine is set free. Advantage is taken of this fact in ascertaining the presence of iodine. The most delicate test for it, when uncombined, is the intense blue colour which it strikes with starch; by its means, with due precaution, 1 part of iodine, when dissolved in one million parts of water, may be discovered.

There are various modes of applying this test: the simplest consists in mixing a little cold starch paste with the liquid which is suspected to contain iodine; if it be present in an uncombined form, a beautiful blue colour shows itself. If the iodine be in combination, this colour does not appear until a drop of chlorine water or of solution of bleaching powder be added to set the iodine free. An excess of chlorine must be avoided, as it forms chloride of iodine, and prevents the action of the test: David Price recommends the use of a solution of nitrite of potash as a substitute for the chlorine, the liquid to be tested being slightly acidulated: no inconvenience arises from the presence of the nitrite in slight excess. The colour fades away if the solution be heated, but it is partially restored as the temperature falls. Solutions of the alkalies, as well as of sulphurous acid, sulphuretted hydrogen, and reducing agents generally, destroy the colour. As starch paste cannot be long kept without undergoing decomposition, it is often convenient to substitute for the freshly made paste, paper which has been smeared with the starch, and allowed to become dry. If kept in a dry place, such paper may be preserved for an indefinite length of time, and is ready for use at any moment.

(332) Hydriodic Acid ($HI=128$); *Sp. Gr.* 4·443; *Comb.*

Vol. 4.—By heating iodine in hydrogen, the volume of the gas becomes doubled, and a colourless acid gas is produced, but it is never prepared for use in this manner. A better mode is the following: —Place in a small retort 10 parts of iodide of potassium with 5 of water, and 20 of iodine; then drop in cautiously 1 part of phosphorus cut into small fragments, and apply a gentle heat. Hydriodic acid gas will be extricated abundantly, and may be collected, by displacement, in dry bottles. The result of the reaction is explained by the following equation:—

$$\underbrace{2\,KI}_{\text{Iodide of potassium.}} + \underbrace{5\,I}_{\text{Iodine.}} + \underbrace{P}_{\text{Phosphorus.}} + \underbrace{8\,HO}_{\text{Water.}} \text{ yield } 2\,\underbrace{KO, HO, PO_5}_{\text{Phosphate of potash.}} + 7\,\underbrace{HI.}_{\text{Hydriodic acid.}}$$

Another but inferior method consists in heating 4 parts of iodine with 6 parts of crystallized sulphite of soda and 1 part of water, when a decomposition occurs analogous to that which attends the formation of hydrobromic acid by a similar process (329).

Hydriodic acid gas is not combustible, nor does it support combustion. It fumes in the air, and possesses a powerfully acid irritating odour. It is reduced under strong pressure to a yellowish liquid, which freezes at 60°. Water dissolves the gas with great avidity.

A solution of hydriodic acid may be easily prepared by suspending iodine in water, and transmitting a current of sulphuretted hydrogen gas through the mixture until the brown colour of the iodine disappears; sulphur is deposited in abundance, and hydriodic acid is formed. The liquid gradually becomes clear if left at rest; it may then be decanted from the precipitated sulphur: the decomposition consists simply in the displacement of the sulphur by the iodine; $HS + I$ becoming $HI + S$. This liquid may be concentrated till it acquires a density of 1·7, when it consists of $HI + 11HO$ (Bineau*.) It then distils unchanged at 262°. It is a powerful acid, and dissolves iodine freely, forming a brown solution: by exposure to the air, especially if placed in a strong light, it absorbs oxygen, water is formed, and the liquid becomes brown from the liberation of iodine. Chlorine effects its instant decomposition, whether it be in the gaseous form or in solution. Mercury decomposes it gradually, and combines with its iodine.

The composition of hydriodic acid may be ascertained by heating potassium in a measured volume of the gas. Iodide of potas-

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* Probably both in this case, and in the analogous one of the solution of hydrobromic acid, the constancy of the boiling point, as well as the apparent definite character of the hydrate, is accidental, and dependent upon causes similar to those traced in hydrochloric acid by Roscoe and Dittmar (p. 112).

sium is formed, and hydrogen remains equal in bulk to half the acid gas employed, consequently its composition may be thus represented:—

			By weight.		By vol.		Sp. gr.
Iodine	I	=	127	or 99·21	2	or 0·5	= 4·378
Hydrogen ...	H	=	1	0·79	2	0·5	= 0·034
Hydriodic acid	HI	=	128	100·00	4	1·0	= 4·412

Iodides.—The iodides of the metals are all solid at ordinary temperatures; they are less fusible and volatile than the corresponding chlorides and bromides. The iodides of gold, silver, platinum, and palladium are decomposed by heat alone, whilst the metals are left in a state of purity; but most of the iodides are converted into oxides when heated in the air,—the oxygen displacing the iodine. All the iodides, whether solid or in solution, are decomposed by chlorine and bromine, as well as by nitrous acid and concentrated nitric acid, with liberation of iodine. Water dissolves the greater number of the metallic iodides freely; some of them are insoluble, and exhibit colours of great brilliancy. The soluble iodides of the metals may be obtained by the direct combination of hydriodic acid with the metallic oxide, or by the action of iodine and water upon the metal itself. These iodides, when in solution, are characterized by the reaction with starch already mentioned. With a solution of corrosive sublimate (chloride of mercury, HgCl) they give a beautiful salmon-coloured precipitate, which almost immediately changes to a brilliant scarlet: this is the iodide of mercury; it is soluble in excess both of iodide of potassium and of corrosive sublimate. Subnitrate of mercury gives a green precipitate in solutions of the soluble iodides. With nitrate of lead they yield a bright yellow precipitate of iodide of lead, which is slightly soluble in boiling water, especially if the lead salt be present in excess; on cooling, the iodide of lead is deposited in very beautiful silky scales. With nitrate of silver a buff-coloured iodide of silver, nearly insoluble in ammonia, is formed. If a mixture of protosulphate of iron and sulphate of copper be added to a solution of any iodide, a white subiodide of copper is precipitated. With chloride of gold the iodides give a lemon-yellow precipitate; and with salts of palladium a brown iodide of palladium is produced, which is sometimes used for ascertaining the quantity of iodine present in a solution in which it occurs mixed with chlorine, since chloride of palladium is freely soluble in water (446 *a*).

(333) OXIDES OF IODINE.—Iodine has a more powerful affinity for oxygen than either chlorine or bromine, and forms with it two well-defined acids, viz., the iodic acid and the periodic acid, be-

sides some other oxides but imperfectly known. The composition of the two acids is the following:—

			In 100 parts.	
			Iodine.	Oxygen.
Iodic acid ...	$IO_5 = 167$	or	$76{\cdot}04$ +	$23{\cdot}96$
Periodic acid ...	$IO_7 = 183$	or	$69{\cdot}39$ +	$30{\cdot}61$

Iodic Acid ($IO_5 = 167$, or $3IO_5$).—This acid corresponds in composition to chloric and bromic acids. It may be prepared in several ways. 1.—It may be procured by long boiling of iodine in concentrated nitric acid. 2.—Equal parts of chlorate of potash and iodine may be mixed with 5 parts of water and a little nitric acid; chlorine is thus evolved in abundance, whilst iodate of potash is formed and dissolved in the liquid: the chloric acid which is set free in the first instance by the nitric acid imparts its oxygen to the iodine, chlorine gas escaping, while the iodic acid liberates a fresh portion of chloric acid from the chlorate, and this undergoes a similar decomposition (Millon). 3.—Liebig's plan of preparing iodic acid consists in suspending iodine in water, and transmitting through it a current of chlorine gas till the iodine is dissolved; the liquid is then neutralized by carbonate of soda, when a copious effervescence ensues, attended by a precipitate of iodine, which may be again treated similarly by chlorine. In this case the chlorine combines directly with the iodine and forms terchloride of iodine, which is dissolved by water unaltered. It is decomposed on the addition of the alkali in the following manner:—

$$5\underbrace{ICl_3}_{\text{Terchloride of iodine.}} + \underbrace{18\,(NaO, CO_2)}_{\text{Carb. soda.}} = 15\underbrace{NaCl}_{\text{Chlor. sodium.}} + \underbrace{3\,(NaO, IO_5)}_{\text{Iodate of soda.}} + 2\underbrace{I}_{\text{Iodine.}} + 18\underbrace{CO_2}_{\text{Carb. acid.}}$$

The neutralized liquid contains iodate of soda and chloride of sodium. Chloride of barium is next added; an abundant precipitate of iodate of baryta, which is but sparingly soluble, is formed; this is washed from adhering salts, and is decomposed by a quantity of sulphuric acid just sufficient to combine with the baryta: iodic acid is dissolved by the water, whilst the insoluble sulphate of baryta is separated.

Iodic acid may be obtained by spontaneous evaporation of its aqueous solution in crystals composed of 3 (HO,IO_5): at a temperature of 266° it loses two thirds of its water, and becomes $HO,3IO_5$; by a further heat of 360° it is rendered anhydrous, and at about 700° it is decomposed into iodine and oxygen. Its solution is destitute of odour, and has a sour, astringent taste: many organic bodies decompose it, and owing to this circumstance litmus paper is first reddened and afterwards bleached by it.

Iodates.—Iodic acid offers some anomalies in its combination with bases. Some iodates contain 1 atom, some 2, and some 3 atoms of acid to 1 atom of base: for example, there are three iodates of potash; they may be represented by the following formulæ:—the normal iodate, KO,IO_5; the biniodate, $KO,HO,2IO_5$: and the teriodate, $KO,HO,3IO_5$. All the iodates are decomposed by heat, and give off oxygen. If the metal have a stronger affinity for iodine than for oxygen, an iodide of the metal is formed; thus iodate of potash (KO, IO_5) becomes $KI+6\ O$: but if the affinity of the metal be greater for oxygen than for iodine, the oxide is left behind: iodate of baryta, for example, is converted into baryta, oxygen gas, and free iodine, the latter escaping with the oxygen in purple vapours; BaO, IO_5 yielding $BaO+5O+I$. The iodates of these alkaline earths, if not heated too strongly, leave a basic periodate, the baryta salt consisting of $5BaO, IO_7$. The aqueous solutions of the iodates are decomposed by sulphurous acid; for example, $KO, IO_5+6\ (HO,SO_2)$ becomes $KI+6\ (HO,SO_3)$; an iodide of the metal is formed, and then the iodine may be discovered by the starch test in the usual way. With the exception of the iodates of the alkalies the iodates are but sparingly soluble. The lime salt retains 6 Aq; those of baryta and strontia, if precipitated from hot solutions, retain 1 Aq, whilst the iodates of lead and silver are anhydrous; iodate of silver is insoluble in diluted nitric acid. Iodic acid forms crystallizable compounds with the sulphuric and many other acids.

(334) Periodic Acid ($IO_7=183$).—This acid has not been procured in the anhydrous form; it corresponds in composition to the perchloric. It is obtained by transmitting a current of chlorine gas through a solution of iodate of soda, which contains caustic soda in the proportion of three atoms of free alkali to 1 atom of iodate of soda; a sparingly soluble basic periodate of soda is formed. The reaction which occurs consists in the decomposition of 2 atoms of soda by 2 of chlorine, chloride of sodium being formed, whilst the 2 atoms of oxygen combine with the iodic acid to form the periodic acid; the latter combines with a second atom of soda, and forms the basic periodate of soda, as explained by the following symbols:—

$$\overbrace{NaO, IO_5}^{\text{Iodate of soda.}} + \overbrace{3\ (NaO,HO)}^{\text{Soda.}} + \overbrace{2\ Cl}^{\text{Chlorine.}} = \overbrace{2\ NaO, IO_7}^{\text{Subperiodate of soda.}} + \overbrace{2\ NaCl}^{\text{Chlor. sodium.}} + \overbrace{3\ HO}^{\text{Water.}}$$

The basic periodate of soda, which when crystallized contains ($2\ NaO, IO_7+3\ HO$) is dissolved in diluted nitric acid, and precipitated by the addition of nitrate of silver; the periodate of

silver is then dissolved in boiling nitric acid; a normal periodate of silver (AgO, IO_7) crystallizes as the liquid cools, and this salt when treated with water is decomposed into basic periodate of silver, which is insoluble, and periodic acid, which is dissolved. By evaporation of the solution the periodic acid may be obtained in deliquescent oblique rhombic prisms, which contain 5 atoms of water, and are somewhat soluble in alcohol and in ether. The periodates are most of them sparingly soluble in water, but are dissolved freely by diluted nitric acid. The normal soda salt (NaO, IO_7) causes, with solutions of normal salts of baryta, a precipitate of a basic periodate ($5\ BaO, 2\ IO_7 + 5\ Aq$). Analogous precipitates are formed with salts of lime, of lead, or of silver, whilst the liquid becomes acid. The basic silver salt is pale yellow ($2\ AgO, IO_7 + 3\ Aq$) if precipitated from cold, but red ($2\ AgO, IO_7 + Aq$) if from hot solutions.

(335) Chlorides of Iodine.—Two compounds of iodine with chlorine, a protochloride (ICl) and a terchloride (ICl_3) may be obtained.

The *protochloride* is a very irritating, volatile, yellowish-brown liquid, which is obtained by distilling 1 part of iodine with 4 parts of chlorate of potash; the distilled chloride of iodine is soluble, apparently without change, in water, in alcohol, and in ether. This chloride when hot dissolves iodine readily, and deposits it in beautiful crystals.

Terchloride of iodine is procured by acting upon iodine with excess of dry chlorine gas. It forms magnificent ruby red crystals, which undergo spontaneous sublimation in closed bottles: the vapour is extremely irritating to the eyes. If exposed to the air it attracts moisture, and is dissolved by water without experiencing decomposition. Alkaline solutions decompose it, and iodine is precipitated as in Liebig's method of preparing iodic acid (333).

Bromides of Iodine.—Iodine also combines with bromine, and forms compounds with it which are possessed of properties similar to those of the chlorides of iodine.

(336) Iodide of Nitrogen? (NHI_2).—This substance may be obtained as a black powder by digesting iodine for half an hour in a cold solution of ammonia. The brown supernatant liquid, which contains an excess of iodine held in solution by iodide of ammonium, is decanted, and the insoluble powder is placed upon filtering paper in quantities of a grain or less, and allowed to dry spontaneously. It may also be prepared by mixing alcoholic solutions of iodine and ammonia, and diluting with water, when

it falls as a black powder which may be washed with an aqueous solution of ammonia. When dry, it explodes upon the slightest touch, and indeed it often detonates without any assignable cause; the explosion is remarkably sharp and sudden, fumes of iodine are produced, and a faint light is emitted.

The experiments of Bineau, the results of which have been subsequently confirmed by Gladstone, have shown that this detonating compound is not a mere iodide of nitrogen, but that it contains hydrogen also, having the formula NHI_2. The mode of its preparation admits of easy explanation by the following equation: $4\ I + 3\ H_3N = 2\ (H_4NI) + NHI_2$, the reaction of 4 atoms of iodine upon 3 of ammonia producing 2 of iodide of ammoninm, and 1 atom of the detonating substance. Bunsen assigns to the compound obtained by precipitating an alcoholic solution of iodine with ammonia the formula $(NH_3,\ NI_3)$, but it is more probable that the composition attributed to it by Bineau (*Ann. de Chimie*, III. xv. 71) is correct.

Iodide of nitrogen becomes slowly decomposed in water; ammonia retards, but potash and the acids accelerate the decomposition; chlorine, bromine, and strong nitric acid, destroy it rapidly; sulphuretted hydrogen also effects its decomposition quietly but completely. The results of the reaction last mentioned afford a means of ascertaining the relative quantities of nitrogen and iodine contained in the iodide: 1 atom of the black powder, when treated with 4 atoms of sulphuretted hydrogen, furnishes 1 atom of iodide of ammonium, 1 of hydriodic acid, and 4 atoms of sulphur:—

$$NHI_2 + 4\ HS = H_4NI + HI + 4\ S.$$

(336 *a*) *Natural Relations of the Halogens.*—It is impossible not to be struck with the close analogy presented by the three elementary bodies, chlorine, bromine, and iodine, both in their uncombined state and in their compounds: they indeed form one of the best defined natural groups of simple substances. All these elements have the peculiarity of combining with hydrogen in the proportion of 2 volumes of the gas or vapour with 2 volumes of hydrogen; the union occurring without change of bulk, and the compound formed being acid and extremely soluble in water. The intensity of their chemical activity decreases as the combining number increases. When in the liquid form the three elements have the same atomic volume (1468); and when united with the same metal the salts which they furnish are isomorphous; the chloride, the bromide, and the iodide of potassium, for example,

all crystallizing in cubes. Each of these elements also forms a powerful acid with 5 atoms of oxygen.*

At the time that iodine was discovered, chlorine was by most chemists regarded as a compound of muriatic acid and oxygen, and was consequently known as *oxymuriatic acid.* Indeed, most of the reactions which it presented admitted of a simple explanation on this hypothesis, and this circumstance prevented chemists from adopting generally the views which had a short time previously been put forward by Davy, maintaining the elementary nature of chlorine. The discovery of iodine, however, decided them, and assisted materially in fixing the opinion now entertained respecting the compounds of fluorine, the fourth member of the group, and of which our knowledge is in a much less satisfactory condition.

§ IV. Fluorine (F = 19).

Theoretical Density, 1·313 ; *Comb. Vol.,* 2.

(337) Many unsuccessful attempts have been made at various times to isolate fluorine. Its affinities are so powerful, and its action on the human frame is so irritating and deleterious, that little that is satisfactory is known concerning it in its free state. Vessels of fluor-spar are the only ones which have as yet been found capable of withstanding its action. No doubt, however, is entertained of its general nature, since its compounds are closely analogous to the corresponding ones of the three elements which have just been described.

Fluor-spar, or fluoride of calcium (CaF), is the only compound of fluorine which exists native in abundance; and from it all the preparations of fluorine are obtained. Small quantities of fluoride of calcium, are contained in a variety of minerals, particularly in the phosphates of lime and certain kinds of mica. It exists too in minute quantity in the bones of animals, and especially in the teeth.

(338) Hydrofluoric Acid: sometimes incorrectly termed *Fluoric Acid* (HF=20).—*Calcd. Sp. Gr. of Anhydrous Vapour,* 0·689.—Fluorine is not known to form any oxide, but with hydrogen it constitutes a very remarkable acid.

Preparation.—In order to procure hydrofluoric acid in solution

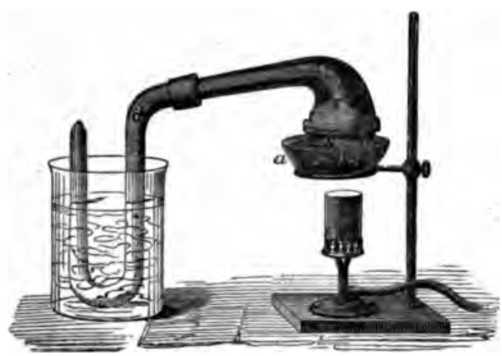
* Nitrogen is remotely connected with this group by the similarity of the nitrates with the chlorates, and of the nitrites with the chlorites: it forms an intermediate link in the natural grouping of the elements between the halogens and the elements belonging to the phosphorus family; its compound with hydrogen (viz., ammonia) presenting some analogies with phosphuretted hydrogen, which will be more fully shown hereafter.

in a concentrated form, 1 part of finely powdered fluor-spar, free from silica and the metallic sulphides, is mixed with 2 or 3 parts of oil of vitriol; at ordinary temperatures no evolution of vapour occurs if the fluor-spar be pure, but a transparent gelatinous mass is formed. On the application of a gentle heat dense acid fumes of an extremely deleterious nature arise, and a reaction takes place similar to that which occurs in the preparation of hydrochloric acid: thus,

$$CaF + HO, SO_3 = HF + CaO, SO_3.$$

Owing to the powerfully corrosive action which this compound exerts upon glass, which it deprives of its silicon, it is necessary always to prepare it in metallic vessels. For ordinary purposes the distillation may be conducted in a leaden retort. For the convenience of removing the charge after the operation is over, it is found advantageous to make the retort in two pieces, a head and a body; the head, *c*, fig. 279, fits accurately by an overlapping grooved joint into the body, *b*. The heat may be conveniently applied in an equable manner by placing the body of the retort in a shallow iron tray, *a*, filled with sand: *d* is the receiver for the acid: it consists of a leaden pipe fitted by grinding to the neck of the retort, and is cooled by immersion in a mixture of ice and salt. When a perfectly pure acid is required, the still must consist of platinum.

FIG. 279.



The concentrated acid, obtained by the foregoing method, was long believed to be anhydrous; but the researches of Louyet (*Comptes Rendus*, xxiv. 434) have proved that it contains water. He distilled it with an excess of anhydrous phosphoric acid: the water was thereby removed, and a colourless gas of an extremely irritating nature was set free; it produced dense fumes on escaping into the air, had but little action on perfectly dry glass, and was rapidly condensed by water. Fremy (*Ann. de Chimie*, III. xlvii. 5) prefers to subject the double fluoride of potassium and hydrogen (KF, HF) to distillation; the salt is first rendered anhydrous

by careful desiccation, and by afterwards applying a strong heat the equivalent of hydrofluoric acid is expelled: by the application of a freezing mixture of ice and salt, the anhydrous acid is said to be obtained in the form of a colourless, mobile, very volatile liquid. Fremy also states that he obtained the anhydrous acid by decomposing fluoride of lead by dry hydrogen. It admits of doubt, however, whether the liquid obtained by either of these processes was really anhydrous; for it is opposed to analogy that hydrofluoric acid should be condensed more readily than hydrochloric acid, which requires a greater pressure to liquefy it than hydrobromic acid, and hydrobromic acid a greater than hydriodic acid, the facility of liquefaction increasing as the combining number of the acid becomes more elevated.

Properties.—The acid obtained by distilling fluor-spar with oil of vitriol is a densely fuming, volatile, colourless liquid, which boils at about 60°, and remains unfrozen at —4°. The preparation of this acid must be conducted with the greatest care, and special provision must be made for carrying off the fumes from the operator. The liquid acid is highly dangerous, from its caustic action upon the skin; the smallest drop occasioning a deep and painful burn. Indeed, it ought never to be preserved in the concentrated form. When poured into water it combines with it with great avidity, and with the evolution of so high a temperature as to produce a hissing noise, resembling that caused by quenching a red-hot iron. In its concentrated form it has a specific gravity of 1·060, but by the addition of water the density may be increased to 1·150, beyond which point further dilution is attended with a regular decrease in density. The acid of sp. gr. 1·150 is a quadrihydrate ($HF+4\,HO$), it boils at 248°, and may be distilled unchanged. Diluted hydrofluoric acid gradually dissolves the metals, excepting platinum, gold, silver, lead, and mercury, extricating hydrogen. Potassium if thrown into the strong acid decomposes it with explosion.

Hydrofluoric acid is easily recognised by its corrosive action upon glass. In order to detect a fluoride in a compound which is suspected to contain it, the material is reduced to a fine powder and mixed in a platinum capsule with strong sulphuric acid; a slip of glass is warmed and rubbed over with bees' wax so as to coat it uniformly; a few characters are next traced with a point through the wax, so as to expose a portion of the glass; this etching is then inverted over the platinum capsule, which is gently warmed for a few minutes, and the glass is cooled, if necessary, with a piece of moistened filtering paper, in order to prevent the wax

from being melted. If fluorine be contained in the mixture, the glass, on cleaning off the wax with a little oil of turpentine, will be found to be corroded in the parts exposed: if the traces be very faint, they may be rendered visible by breathing upon the surface of the plate.

A weak solution of hydrofluoric acid is often employed for etching on glass, with advantage: in this way, for instance, the graduations on the glass stem of a thermometer may be made with great precision and facility; the glass tube is first coated with engravers' etching varnish, the divisions are traced through the varnish with a fine point, and the tube is plunged into a long leaden tube filled with the diluted acid; in the course of a few minutes the scale is permanently engraved.

Fluorides.—The compounds of the metals with fluorine fuse easily on the application of heat, and hence the origin of the terms *fluor*-spar and fluorine (from *fluo*, 'to flow'). A large number of them are insoluble, or only sparingly soluble in water. They are all decomposed when heated with oil of vitriol, and evolve hydrofluoric acid; but they are not attacked by nitric acid. The solutions of the soluble fluorides corrode the glass vessels in which they are contained: they give no precipitate with nitrate of silver, since fluoride of silver is soluble; but with salts of lead, barium, magnesium, and calcium, insoluble precipitates, consisting of the fluorides of these metals, are produced. The fluoride of calcium is so transparent as to be perceived with difficulty; but on heating the liquid, or on the addition of ammonia, it is rendered more opaque.

Many metallic fluorides combine with an additional atom of hydrofluoric acid, and form compounds which in many cases may be obtained in crystals that are soluble in water. The double fluoride of potassium and hydrogen (KF, HF) has been already mentioned as a convenient source of concentrated hydrofluoric acid. Double fluorides of the alkaline metals with the fluorides of the electro-negative metals which form acids with oxygen may likewise be obtained with facility. Many insoluble metallic acids, such as the tantalic, titanic, molybdic, and tungstic acids, are thus dissolved by hydrofluoric acid, fluorides of the metals being formed, whilst the oxygen of these compounds produces water with the hydrogen of the hydrofluoric acid: the metallic fluorides so formed are dissolved by the excess of hydrofluoric acid, and give rise to new compound acids. Titanic acid, for instance, is thus converted into fluotitanic acid; $TiO_2 + 3\ HF$ becoming $HF, TiF_2 + 2\ HO$.

Hydrofluoric acid, when mixed with nitric acid, readily dissolves silicon which has not been strongly ignited; but it is

remarkable that the mixture does not dissolve either gold or platinum.

Numerous other compounds of fluorine have been prepared, but they are not of sufficient practical importance to require notice here: the compounds which it forms with silicon and with boron will be described hereafter (389, 394).

(339) *Determination of the Combining Number of Fluorine.*— Although the chemist has hitherto been unable to isolate fluorine in a state of purity, yet its combining number has been determined with precision; and the mode of proceeding offers an instructive illustration of the resources of analysis in such a case.

The method of operating is as follows:—Pure fluor-spar is reduced to an impalpable powder, and dried; 100 grains of this powder are accurately weighed into a counterpoised platinum crucible, and sulphuric acid, also perfectly pure, is added in quantity sufficient to reduce the whole to the consistence of cream: after standing for some hours, the excess of acid is expelled by the heat of a lamp: the temperature is raised very cautiously, and the crucible and its contents are finally heated to bright redness. In this operation the whole of the fluorine is expelled in the form of hydrofluoric acid, the calcium combining with the oxygen of the water in the oil of vitriol, whilst the fluorine unites with the hydrogen; the lime thus produced unites with an equivalent of sulphuric acid, and forms sulphate of lime, which remains behind. On weighing the crucible after the experiment is completed, the sulphate of lime will be found to amount to 174·36 grains.

Now it is known that 68 grains of sulphate of lime contain 20 of calcium, 40 of sulphuric acid, and 8 of oxygen; 20 being the combining number of calcium:—

$$\text{but } 68 : 20 :: 174{\cdot}36 : x(=51{\cdot}25);$$

174·36 grains of sulphate of lime must consequently contain 51·25 of calcium; 100 parts, therefore, of fluor spar, if it consist only of fluorine and calcium, must be composed of 51·25 of calcium and 48·75 of fluorine. The combining number of fluorine is then found directly by the following calculation:—

Qty. of calcium in 100 parts.		At. wt. of calcium.		Qty. of fluorine in 100 parts.		At. wt. of fluorine.
51·25	:	20	::	48·75	:	19

The combining number of fluorine is thus ascertained to be 19.

CHAPTER VII.

SULPHUR—SELENIUM—TELLURIUM—PHOSPHORUS.

(339 *a*) *Natural Relations of the Sulphur Group.*—The four substances which will be next described, viz., sulphur, selenium, tellurium, and phosphorus, are characterized by a powerful attraction for oxygen.

Between sulphur, selenium, and tellurium, a marked analogy in chemical character is observable. The properties of selenium are intermediate between those of sulphur and tellurium, which latter presents so much of the external characters and appearance of a metal, that it is usually described with the metals. Amongst the compounds of each of these bodies with oxygen are two acids—one with 2 atoms of oxygen corresponding with sulphurous acid SO_2, and another with 3 atoms of oxygen corresponding with sulphuric acid SO_3. One volume of the vapour of each of these three elements unites with 2 volumes of hydrogen to form 2 volumes of a gaseous compound possessed of feebly acid characters. The atomic volume (1468) of solid sulphur is 101, and that of selenium 103, or nearly identical; but that of tellurium, 128, is one-fourth higher. It may be further remarked that the corresponding compounds of sulphur, selenium, and tellurium are isomorphous. Oxygen also presents a certain analogy with the members of this group, 1 volume of oxygen uniting with 2 volumes of hydrogen to form 2 volumes of steam, and the oxides and sulphides generally exhibit many points of resemblance.

(339 *b*) *Natural Relations of the Phosphorus Group.*—Phosphorus is described here for the sake of convenience, and not because it exhibits any relation to the sulphur group; it has, however, a close connection with arsenic and antimony, two bodies which will be described with the metals.

Phosphorus, arsenic, and antimony are indeed related much in the same way as sulphur, selenium, and tellurium; each of them unites with hydrogen, and forms a gaseous compound in which 6 volumes of hydrogen combine with 1 volume of the vapour of the other element—the compound which is formed occupying the space of 4 volumes—these gaseous compounds exhibiting a tendency to alkalinity. Each of these elements unites with oxygen in the proportion of 1 atom with 3, and 1 with 5 atoms of oxygen, forming compounds in which the acid character is less and less marked as the atomic weight of the combus-

tible element increases. The isomorphous relations of arsenious acid and teroxide of antimony have long been known, and the corresponding tribasic phosphates and arseniates offer some of the most striking exemplifications of isomorphism. Chlorine unites with the members of the group in the proportion of 3 atoms to 1 atom of phosphorus, arsenic, or antimony. Nitrogen, as already pointed out, is connected with the phosphorus group by its combination with hydrogen (H_3N), and by its formation of acids with 3 and with 5 atoms of oxygen. An interesting isomorphous relation exists between the members of the sulphur and those of the phosphorus group; 2 atoms of sulphur being isomorphous with 1 atom of arsenic, as is shown in the correspondence in form between crystals of iron pyrites ($Fe\ S_2$), and those of mispickel (FeS_2, $FeAs$).

The singular numerical relations which Dumas and others have pointed out between the atomic weights of the members composing these groups and those of several other elements equally closely allied, will be discussed at a future point (894).

It will be sufficient here to remark, that in groups of electronegative elements of similar properties it is usually observable that the chemical activity of each element of the group is usually greater, the smaller is its combining number; sulphur, for example, being more active in its chemical relations than selenium, and selenium than tellurium: so again, fluorine is more energetic in its affinities than chlorine, chlorine than bromine, and bromine than iodine. In the metals, or basylous elements, the order of their activity is exactly the reverse; potassium being more active than sodium, and sodium than lithium.

§ I. Sulphur ($S=16$).

Combining Volume below 1500°, $\frac{1}{3}$; *at* 1900°, 1; *Specific Gravity of Vapour,* 6·617 *at* 900° *F.*; *at* 1900° 2·2.*

(340) Most of the sulphur used in England is obtained from Sicily, where it occurs in the native or uncombined state in beds of a blue clay formation, stretching from the southern coast of the island towards the base of Mount Etna. It is also found abundantly in volcanic districts generally, and particularly in

* In Gerhardt's system of notation the atomic weight of sulphur is $S=32$; and he represents sulphurous acid as $SO_2=64$; sulphate of potash as K_2SO_4; sulphuric anhydride as $SO_3=80$; oil of vitriol as H_2SO_4; neutral sulphate of potash as K_2, SO_4; and bisulphate of potash as KH, SO_4. Sulphurous and sulphuric acids are thus regarded as dibasic compounds, and a consistent notation is obtained which has chemical reasons in its support in addition to the simplicity introduced by it into the formulæ. If the reason for doubling the atomic number for sulphur be admitted, the atomic number of selenium and of tellurium must be doubled likewise.

those which border the Mediterranean. Many of the compounds of sulphur with the metals occur in great abundance as natural productions,—especially the sulphides of iron, copper, lead, and zinc. Bisulphide of iron (iron pyrites) furnishes a large proportion of the sulphur consumed in the manufacture of oil of vitriol. Sulphur is still more extensively distributed in the oxidized condition as sulphuric acid, in combination with various earths; the sulphates of lime, of magnesia, baryta, and strontia being abundant natural productions. Sulphur is likewise an essential constituent of many bodies of organic origin; it is, for example, always contained in the albuminoid or proteic compounds (1400).

Properties.—Native sulphur is found either in amorphous masses, or in transparent yellow crystals, the form of which is derived from the octohedron with a rhombic base. The sulphur of commerce is either in the form of a harsh, yellow, gritty powder, known as *flowers of sulphur*, or in round sticks, constituting roll sulphur or common *brimstone*. In the latter condition it is a solid, nearly opaque, brittle substance, of a characteristic yellow colour, with a slight peculiar odour. It is insoluble in water, and is consequently tasteless; it is a bad conductor of heat, and when grasped with a warm hand frequently crackles and falls to pieces from the unequal expansion; it is an insulator of electricity, and becomes negatively electric by friction.

Sulphur is highly inflammable, and when heated in the air it takes fire at between 450° and 500°, burning with a blue flame, and emitting pungent suffocating fumes of sulphurous acid. At 239° it melts, forming a yellow liquid which is less dense than the unmelted sulphur. In closed vessels it may, by a further heat, be distilled, the boiling point being about 824° (Dumas); at this temperature sulphur yields a deep yellow vapour of sp. gr. 6·617: 1 volume of this vapour contains 3 equivalents of sulphur. Bineau found that when sulphur is heated to about 1800° F. the vapour becomes dilated to three times the bulk that should be produced by mere elevation of temperature, and that at this high temperature the volume occupied by an equivalent of sulphur vapour corresponds with that of an equivalent of oxygen; this observation has recently been confirmed by Deville and Debray.

Sulphur combines readily with chlorine, with bromine, and with iodine, especially when the action is favoured by heat. It also enters rapidly into combination with most of the metals, many of which, like copper, iron, and silver, if in a state of fine division, burn vividly when heated in its vapour. The compounds of sulphur with the metals are termed *sulphides*, or *sulphurets*.

Extraction.—Advantage is taken of the volatility of sulphur to purify it from the earthy matters which accompany it in its native state. A rough distillation is performed upon the spot where it is obtained. For this purpose a long brick furnace is constructed so as to contain a double row of upright earthenware retorts, each of a capacity of 4 or 5 gallons; each retort is furnished with a large aperture at the top for charging it with the sulphur, and with a short wide tube, which proceeds from the side at the upper part, and slopes downwards through the walls of the furnace into an earthen receiver of a form similar to that of the retort: from the bottom of the receiver a short pipe carries off the still melted sulphur into a vessel containing water. It is, however, still very impure, and requires a second more careful distillation before it is fit for many of the purposes to which it is applied in the arts. This second distillation is conducted in retorts, generally of iron, furnished with a short, wide, lateral neck; the fumes are received in large chambers of brickwork. If the walls of these chambers be kept cool, and the process be conducted slowly, the sulphur is condensed in powder, and forms 'flowers of sulphur;' but if the fire be urged, and the masonry be allowed to become hot, the sulphur melts, runs down, and is then drawn off into cylindrical wooden moulds, which give it the usual form of roll sulphur.

When sulphur is prepared from pyrites (FeS_2), the mineral is sometimes distilled in closed vessels, and by this means about one-third of the sulphur which it contains is volatilized and condensed, magnetic pyrites, Fe_3S_4, remaining; but it is more usual to conduct the operation in the open air, as a preliminary step in the roasting of copper pyrites to prepare it for smelting. Huge heaps of the ore are arranged in the form of a truncated square pyramid, the base of which is about 30 feet in the side. A layer of powdered ore is placed at the bottom, and over this one of brushwood; in the centre is constructed a wooden chimney, which communicates with air-ways left between the fagots; fragments of ore are now piled up until the heap is about 8 feet high, and the whole is lastly covered, for a depth of 12 inches, with a layer of powdered ore. Such a heap contains upwards of 2000 tons of pyrites, and will furnish about 20 tons of sulphur. When the construction of the heap is complete, the fire is kindled in the centre by dropping lighted fagots down the chimney; in the course of a few days the heat becomes diffused throughout the mass, and sulphur begins to ooze from the surface. When this is observed, numerous hemispherical wells or excavations, fitted with covers, are made in the

superficial layer of ore for the reception of the sulphur; into these cavities it drains, and is daily ladled out and cast into moulds. The process of roasting such a heap occupies five or six months.

Uses.—Sulphur is extensively employed in the arts; from its ready inflammability it is used to facilitate the combustion of many bodies, as in the preparation of matches; and large quantities are consumed in the manufacture of gunpowder. It is employed to some extent as a medicine, especially in certain forms of cutaneous disease; when converted into sulphurous acid it is applied to the bleaching of silks and flannels; but its chief consumption is in the production of sulphuric acid.

(341) *Various forms of Sulphur.*—Sulphur has been already pointed out (84) as affording a striking illustration of the occurrence of allotropy: it may be obtained in several distinct modifications of form, or in different allotropic states.

The first form, which has been distinguished by the symbol S_α, is the native crystal of sulphur, the octohedron with a rhombic base. It may be obtained artificially by allowing the solution of sulphur, in chloride of sulphur, or in bisulphide of carbon, to evaporate spontaneously. It is semitransparent, of an amber yellow colour, and has a density of 2·05. Its crystals undergo no change in the air: they fuse at 239° F.

The second variety, S_β, is obtained by melting a few pounds of sulphur, and allowing it to solidify on the surface; if the crust be pierced with a hot wire, the still fluid portion may be poured off; and the solid mass beneath will be found to be lined with transparent brownish-yellow needles, belonging to the oblique prismatic form; these have a specific gravity considerably less than S_α, viz., 1·98, the density of ordinary roll sulphur. According to Brodie, it melts at 248°. This form is not permanent in the air: in a few days, or (if the surface of the crystals be scratched) in a few hours, the transparency disappears, and although to the eye the crystals retain their prismatic outline, they lose their coherence, and an opaque crumbling mass is produced, consisting of minute rhombic octohedra. On the other hand, if an octohedron of S_α be placed in a liquid, the temperature of which is slowly raised to a point between 220° and 230°, it loses its transparency, owing to the formation of prismatic crystals.

Mitscherlich has ascertained that in the passage of the prismatic into the octohedral form, an amount of heat is emitted which would raise the temperature of an equal weight of water 4·09° F. This conversion of the prismatic into the octohedral variety may be effected suddenly, by immersing the prisms in a

solution of bisulphide of carbon, even when this solvent is already saturated with sulphur (*Ann. de Chimie*, III. xlvi. 124).

The third variety, S_γ, is even more remarkable than the preceding forms: it is produced by the action of a still higher temperature. The influence of heat upon sulphur is indeed very peculiar. It begins to melt at about 239°, and between 250° and 280° it forms a yellow, transparent, and tolerably limpid liquid: as the temperature rises, the colour deepens, it becomes brown, and at last nearly black and opaque. At 350° these changes are very decided; it gradually becomes more and more viscid; the temperature at this point for a while becomes stationary, notwithstanding continued accessions of heat from without, so that heat is becoming latent, as in the analogous case of the melting of ice. After a while, if the application of heat be steadily continued, the temperature again rises, and when it has attained to nearly 500° the sulphur once more liquefies, though it never becomes as fluid as at the temperature of 240° when first melted. If now suddenly cooled by pouring it in a slender stream into cold water, a soft tenacious mass is produced, which may be drawn out into elastic threads. The colour of the cooled threads varies from a pale amber to a deep brown, becoming darker in proportion to the elevation of temperature which it has experienced. Magnus has shown (*Poggendorff's Annal.*, xcii. 308) that this deepening in colour of the melted sulphur is due to the formation of another modification of sulphur, which is black; the more frequently the sulphur is heated up to about 600°, and then suddenly cooled, the larger is the quantity of this black sulphur which is formed: the details of the process required for insulating it are given at length in the memoir above referred to. A red variety of sulphur was also obtained by Magnus, which Mitscherlich proved to be produced only when a minute quantity of some fatty body was present. Ductile sulphur has a sp. gr. of only 1·957. In a few hours it becomes yellow and opaque, and returns to the brittle form, giving out again the heat which it had absorbed; it also increases in density, the greater part of it assuming the form of S_α. If this ductile sulphur be heated to 212°, it suddenly returns to the brittle condition, the temperature rising to 230° during the change.

Crystalline sulphur, either S_α or S_β, is soluble in about 3 times its weight of bisulphide of carbon; it is also freely dissolved by the dichloride of sulphur: by spontaneous evaporation of these liquids the sulphur is left in octohedra. Benzol is also an excellent solvent for sulphur, especially when heated. Boiling oil of turpentine likewise dissolves sulphur freely, and retains 1·5 per cent. of it on cool-

ing: as the liquid cools, the sulphur crystallizes, first in the prismatic form, S_β, afterwards as the temperature continues to fall, octohedra, S_α, are produced. Vitreous sulphur, S_γ, is but partially soluble in bisulphide of carbon; and after it has lost its vitreous and tenacious character by exposure to the air it is not wholly changed into the ordinary form of sulphur, for when treated with bisulphide of carbon a pale buff-coloured powder of sp. gr. 1·955 is left; it may, by fusion, be reconverted into ordinary sulphur, soluble in bisulphide of carbon. If vitreous sulphur be left in contact for 24 hours with an aqueous solution of sulphuretted hydrogen, it is changed iuto the amorphous form. The amorphous sulphur, which is insoluble in bisulphide of carbon, is much more readily oxidized when heated with nitric acid than the crystalline soluble modification. If maintained at 230° for some time, it gradually passes into the octohedral modification, evolving heat during the change.

(341*a*) According to Berthelot (*Ann. de Chimie*, III. xlix. 435) there are among the various modifications of which sulphur is susceptible, two principal forms which are more stable than the rest. These are the *octohedral*, or, as he terms it, the *electronegative* variety, the most permanent condition of sulphur, and a pulverulent, or *electropositive* form, which is insoluble in bisulphide of carbon.

In the so-called electronegative or octohedral condition it is soluble in bisulphide of carbon. This variety is deposited at the positive electrode of the voltaic battery during the electrolysis of an aqueous solution of sulphuretted hydrogen. To this variety the prismatic form, and the white precipitate obtained from the alkaline polysulphides by the addition of an acid, belong. It is this form which is always deposited from cold solutions of sulphur; whether the solvent be alcohol, benzol, bisulphide of carbon, or chloride of sulphur.

The electropositive condition is obtained when sulphur is separated from its combinations with elements which like oxygen, bromine, and chlorine, are more electronegative than sulphur itself. The most stable variety is that obtained by treating flowers of sulphur first with bisulphide of carbon, then with alcohol, and then a second time with the bisulphide; it is somewhat less stable when procured from the dichloride of sulphur by decomposing it with water; if the precipitate thus occasioned be purified by digestion in bisulphide of carbon, a yellow, or orange-yellow, amorphous powder is procured. If this powder be heated to 572°, then suffered to cool very slowly, and submitted to 2 or 3 successive sublimations at a low temperature, it becomes converted into the

electronegative condition, and is rendered entirely soluble in bisulphide of carbon. The electropositive variety may also be slowly converted into the electronegative form by contact with certain electropositive substances, as by digestion for some days in a solution of liquid ammonia, in one of sulphide of sodium, or in one of bisulphite of potash, in which case a portion of the sulphur becomes dissolved, and the remainder is rendered soluble in bisulphide of carbon. Electropositive sulphur is deposited at the negative electrode of the battery during the electrolysis of sulphurous or sulphuric acid. Other modifications of the insoluble form of sulphur, which pass with greater facility than the foregoing one into the soluble variety (for example, by exposure to 212° for some hours), may be obtained by decomposing the oxidized compounds of sulphur, such as the hyposulphites, by acids. The black sulphur of Magnus is also insoluble in bisulphide of carbon.

All the varieties of sulphur are soluble to a small extent in boiling anhydrous alcohol, the electropositive varieties becoming modified as they are dissolved: the hot solution as it cools deposits minute transparent prismatic crystals of the electronegative variety. Chloroform and ether dissolve sulphur less freely than alcohol.

When sulphur is distilled in small quantities, and received into vessels in which the temperature is not considerably reduced, the sulphur is condensed in red drops, which remain liquid for many hours. Sulphur is also frequently liberated in the ductile form from the native sulphides of the metals during their solution in *aqua regia*, and from the hyposulphites when decomposed by concentrated hydrochloric acid. When nitric acid is used, the sulphur is separated in solid flocculi.

(342) COMPOUNDS OF SULPHUR WITH OXYGEN.—Sulphur forms numerous compounds with oxygen: two of them (sulphurous acid and sulphuric acid) have been long known and employed on a large scale in the arts; the others are less important, and of comparatively recent discovery. These acids of sulphur are interesting, inasmuch as they exhibit a combining ratio different from any which we have as yet considered, and they show the application of the law of multiple proportions to the case of the sulphur, as well as to that of the oxygen which they contain.

The following table exhibits the composition of the various combinations of sulphur with oxygen, the existence of which is at present known:—

Oxides of Sulphur.			In 100 parts. Sulphur.	Oxygen.
Sulphurous acid . . .	SO_2	= 32	50·00	50·00
Sulphuric acid . . .	SO_3	= 40	40·00	60·00
Hyposulphurous acid . .	S_2O_2	= 48	66·66	33·34
Hyposulphuric acid . . .	S_2O_5	= 72	44·45	55·55
Trithionic acid	S_3O_5	= 88	54·55	45·45
Tetrathionic acid . . .	S_4O_5	= 104	61·53	38·47
Pentathionic acid . . .	S_5O_5	= 120	66·66	33·34

The five acids last enumerated have never been procured in the anhydrous form.

We will examine first the sulphurous acid, then the sulphuric acid, and will pass slightly over the other acids, the compounds of which, with the exception of some of the salts of hyposulphurous acid, have as yet received no practical applications.

(343) SULPHUROUS ACID, or *Sulphurous Anhydride* $(SO_2)_2$, or $(SO_2=32)$; *Comb. Vol.*, 2; *Sp. Gr. of Gas*, 2·247; *of Liquid*, 1·38, 9 at 60°; *Melting Pt.*,—105°; *Boiling Pt.*, 17·6° Pierre, 14° Faraday.—Sulphur burns in oxygen with a lilac-coloured flame, and produces a permanent gas; after the combustion has terminated, and the gas has been allowed to regain its original temperature, the bulk of the gaseous products is found to be the same as before the experiment, but the density of the gas is doubled. This experiment furnishes an easy proof of the composition of the acid; for it is thus shown to contain equal weights of sulphur and of oxygen. Sulphurous acid is the sole product if the oxygen be dry.

The composition of sulphurous acid may be represented in the following way:—

			By weight.		By volume.			Sp. gr.
Sulphur	S	=	16 or	50	2 or	1·0	=	1·1056
Oxygen	O_2	=	16	50	2	1·0	=	1·1056
Sulphurous acid.	SO_2	=	32	100	2	1·0	=	2·2112

Properties.—This gas has a pungent suffocating odour, like that of burning sulphur, and in a concentrated form it is quite irrespirable; but if breathed in a diluted form it produces the symptoms of ordinary catarrh. It is not inflammable, but quickly extinguishes the flame of burning bodies. Sulphurous acid is freely soluble in water, which, according to Bunsen, takes up, at 32°, 68·8 times its bulk of the gas; 43·5 times its bulk at 59°; and 32 at 75°: the liquid has a taste and smell similar to that of the gas; the solution gradually absorbs oxygen from the air, and becomes converted into sulphuric acid. A crystalline hydrate of sulphurous acid ($SO_2 + 15\ HO$; Schoenfeld) may also be obtained at a low temperature; at 40° this hydrate melts and is decomposed.

Owing to the solubility of sulphurous acid in water, the gas must always be collected either over mercury, or in dry bottles by displacement: from the high density of the gas (double that of oxygen), the latter method is easily applied.

Preparation.—1. When required in a pure state, sulphurous acid is always prepared by depriving oil of vitriol of part of its oxygen. In order to effect this, two or three ounces of sulphuric acid in a concentrated form may be boiled in a glass retort upon half an ounce of copper clippings or of mercury. Part of the acid gives up 1 atom of its oxygen to each atom of the metal; the oxide thus produced combines with an atom of the undecomposed acid, whilst an atom of sulphurous anhydride is set free for each atom of the sulphate formed. The reaction in the case of copper may be seen in the following equation: $Cu + 2\ (HO, SO_3) = CuO, SO_3 + SO_2 + 2\ HO$. The gas must be washed by allowing it to bubble up through a bottle containing a small quantity of water, which retains sulphuric acid and any impurities which might be mechanically suspended in the gas.*

2.—Sulphuric acid may be more economically deoxidized by means of charcoal or dry saw-dust, but the gas in this case is accompanied by one half its volume of carbonic acid; $C + 2\ (HO, SO_3) = 2\ SO_2 + CO_2 + 2\ HO$. For most purposes, however, such as the preparation of the alkaline sulphites, the presence of carbonic acid is unimportant. In cases where carbonic acid is objectionable, sulphur may be advantageously substituted for charcoal in the preceding operation, using 1 part of sulphur and 12 of oil of vitriol, the evolution of a pure gas taking place steadily and with great uniformity.

3.—Sulphurous acid may also be procured readily by heating in a flask an intimate mixture of 4 parts of flowers of sulphur and 5 of finely powdered peroxide of manganese, sulphurous acid and sulphide of manganese being produced; $2\ S + MnO_2 = SO_2 + MnS$. A result somewhat similar is obtained by heating a mixture of 3 parts of black oxide of copper with 1 part of sulphur; $2\ CuO + S_2$ becoming $Cu_2S + SO_2$.

Sulphurous acid is emitted abundantly from the craters of volcanoes, and it is occasionally met with in solution in the springs of volcanic districts.

Sulphurous anhydride, by transmission through a tube surrounded by a mixture of ice and salt, may be condensed to a colourless, transparent, limpid liquid, which dissolves bitumen; it

* According to Maumené, a certain quantity of the disulphide of copper, Cu_2S, is also produced during this operation, after which a mixture of sulphide and oxysulphide of copper is also formed.

freezes at -105°, forming a transparent, colourless, crystalline solid, heavier than the liquid; in closed tubes, at 60° it exerts a pressure of 2·54 atmospheres. Fig. 280 shows a method of lique-

FIG. 280.

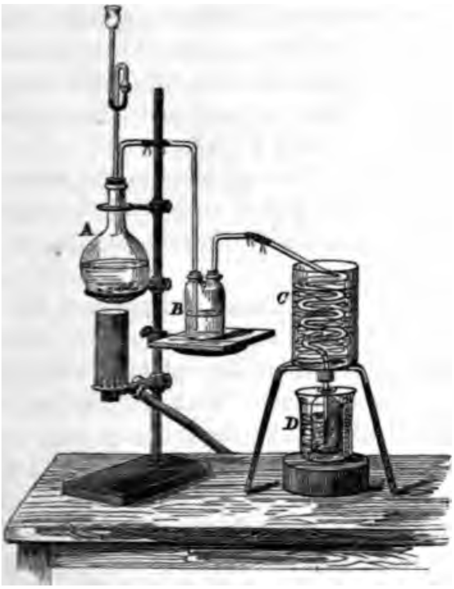


FIG. 281.

fying sulphurous anhydride. The gas is generated in the flask, A, washed and dried by means of concentrated sulphuric acid placed in the bottle, B, transmitted through the pewter worm, C, which is surrounded by a freezing mixture of ice and salt, and collected in the receiver, D, which is also cooled by a freezing mixture; the liquefied compound is stored up for use in small tubes, one of which is shown at E, fig. 281: the tube having been placed in the freezing mixture, the acid is poured into it through a small tube funnel, and the liquid is preserved by drawing off and sealing the tube at the narrow portion in the flame of the blowpipe, whilst the receiver still remains in the freezing mixture.

Uses.—Sulphurous acid possesses considerable bleaching powers, and is extensively employed in bleaching straw and wool. The articles to be bleached are moistened, and suspended in closed chambers in which sulphur is burned in an open dish; the sulphurous acid is absorbed by the damp goods, and their colour is discharged. The gas appears to act by forming colourless compounds with certain colouring matters. It does not, like chlorine, decompose the colouring matter; for the sulphurous acid may either be expelled by a stronger acid, or it may be neutralized by

an alkali, and the colour will be restored : the reproduction of the yellow colour in new flannel, when it is washed with an alkaline soap for the first time, affords a practical illustration of the effect of an alkali upon goods which have been bleached by sulphurous acid. Sulphurous acid is also highly valuable as a disinfecting agent. It is a powerful antiseptic. Meat which has been exposed to the action of the gas, and then sealed up in metallic canisters filled with nitrogen to which a little deutoxide of nitrogen has been added to remove the last traces of oxygen, may be preserved fresh for years.

It is, however, principally as a preliminary step in the manufacture of oil of vitriol that sulphurous acid is made upon the large scale, and in this case it is always obtained by burning sulphur, or a metallic sulphide, in air.

Sulphites.—Sulphurous acid is a weak acid, and presents considerable analogy to carbonic acid in its mode of combining with bases; according to Muspratt's observation, the sulphites and the carbonates are in many cases isomorphous. With the alkalies it forms two kinds of salts, one of which, like the ordinary sulphite of soda ($NaO, SO_2 + 7Aq$), contains 1 equivalent of the acid to 1 of alkali, while the other class, represented by the acid sulphite of potash ($KO, HO, 2\ SO_2$) contains 2 equivalents of acid to 1 of water and 1 of alkali.* The sulphites of the alkalies are the only ones which are freely soluble in water; but those of baryta, strontia, and lime are dissolved to some extent by an aqueous solution of sulphurous acid. Many of the sulphites are decomposed by a strong heat, the acid being gradually expelled. They are also decomposed by sulphuric or by hydrochloric acid, with extrication of sulphurous acid, which is known by its peculiar and pungent odour. The best test for detecting small traces of sulphites consists in the addition of a fragment of zinc and a drop or two of hydrochloric acid to the solution; the sulphurous acid is deoxidized, the sulphur combines with hydrogen, and sulphuretted hydrogen is given off; the gas last named may be detected by suspending a piece of paper moistened with a solution of acetate of lead, in the upper part of the vessel, which should be closed by a glass plate. Salts of silver in solution give a white precipitate with solutions of the soluble sulphites; the precipitate is soluble in excess of the sulphite, and is partially reduced to metallic silver when the liquid is boiled: a characteristic reaction is the formation with chloride of barium of a white precipitate of sulphite of

* If it be conceded that sulphurous acid is dibasic, sulphite of soda would be represented by the formula, $2\ NaO, S_2O_4 + 14\ Aq$, and the acid sulphite of potash by KO, HO, S_2O_4.

baryta, which is soluble in hydrochloric acid, but gives a white precipitate of sulphate of baryta on the addition of a solution of chlorine, of iodine, or of bleaching powder. The sulphites, when moist, absorb oxygen from the air; and solutions of these salts are often used as deoxidizing agents: for example, the salts of sesquioxide of iron are reduced by them to salts of the protoxide. Gold, selenium, and tellurium, are precipitated by them from their solutions in hydrochloric acid in the reduced or metallic form, arsenic acid is reduced to arsenious acid, and chromic acid to a green salt of chromium.

The sulphites are readily formed by transmitting a stream of sulphurous acid through water in which the oxide or the carbonate of the metal is dissolved or suspended, the carbonates being decomposed with effervescence.

Sulphurous acid is by some chemists regarded as the starting point of several combinations belonging to the sulphur series. Without attaching much importance to the probability of this view, we subjoin the following table, which exhibits the supposed relation of some of the more important of these compounds to sulphurous acid:—

Sulphurous acid,	SO_2	
Sulphuric acid,	SO_2,O,	oxide of sulphurous acid.
Chlorosulphuric acid,	SO_2Cl,	chloride of ditto.
Iodosulphuric acid,	SO_2I,	iodide of ditto.
Nitrosulphuric acid,	SO_2NO_2	
Hyposulphurous acid,	SO_2,S,	sulphide of ditto.

(344) SULPHURIC ACID ($HO, SO_3=9+40$).—This substance, which in its hydrated form constitutes one of the most important products of chemical manufacture, is made in enormous quantities. In Great Britain alone upwards of 100,000 tons are annually consumed. The acid is occasionally met with in thermal springs, uncombined with bases. When united with lime, baryta, magnesia, and some other oxides, it forms an abundant constituent of the crust of the earth.

Preparation.—When sulphur is boiled in *aqua regia*, or in concentrated nitric acid, it is gradually oxidized and converted into sulphuric acid; but this method is never employed, excepting for experimental purposes in the laboratory. On the large scale it is made by a process first employed by Roebuck, about the year 1746, since which period the mode of conducting it has undergone several modifications and improvements, though in principle it continues to be the same.

The changes which occur in the process are remarkable and instructive. It has been already mentioned, that when sulphur is burned in air or in oxygen, the product is sulphurous acid; this gas, if made to combine with half as much oxygen again as it already contains, is converted into sulphuric acid. Direct union, however, cannot be produced between the two gases; the intervention of some third substance becomes necessary; and if water be presented to them, a very gradual combination occurs. If pure and dry oxygen, mixed with twice its bulk of sulphurous acid, be transmitted over spongy platinum (62) heated in a tube, the two gases combine, and anhydrous sulphuric acid $(SO_3)_2$ is produced. Wöhler has also observed, that the two gases unite rapidly when transmitted through a tube heated to incipient redness, and containing a mixture of oxide of copper and sesquioxide of chromium, obtained by precipitation.

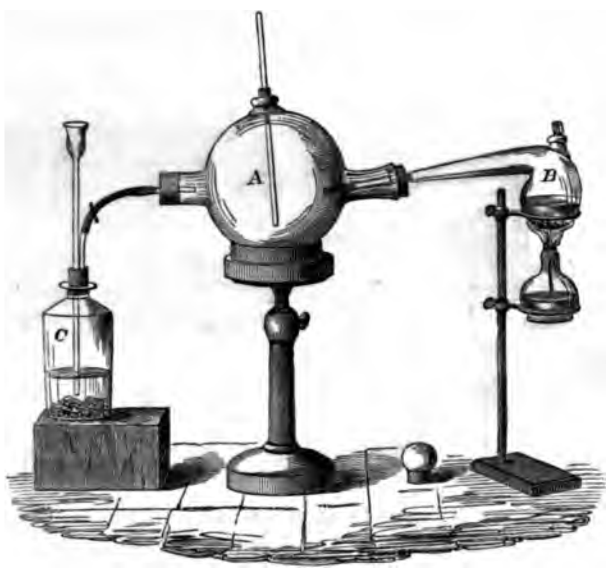
The following table represents the composition of sulphuric acid:—

	Anhydrous.			Monohydrate.		
Sulphur	$S =$	16 or	40	$S =$	16 or	32·65
Oxygen	$O_3 =$	24	60	$O_3 =$	24	48·98
Water				$HO =$	9	18·37
Sulphuric acid	$SO_3 =$	40	100	$HO,SO_3 =$	49	100·00

If moist sulphurous acid mixed with oxygen be presented to deutoxide of nitrogen, or to any other of the higher oxides of nitrogen, this combination may be effected with great rapidity; and further, a small proportion of the deutoxide of nitrogen will suffice to effect the combination of an almost indefinite amount of sulphurous acid and oxygen, if water be also present. Upon these facts the process employed in the manufacture of sulphuric acid is founded. The reaction is easily watched upon the small scale by the following means:—Into a large three-necked receiver, A, fig. 282, filled with atmospheric air, and slightly moistened in the interior, sulphurous acid from the retort, B, and deutoxide of nitrogen from the bottle, C, are made to pass; ruddy fumes of peroxide of nitrogen are immediately formed by the combination of the deutoxide with atmospheric oxygen, and in a few minutes the inner surface of the receiver becomes coated with a white crystalline deposit into the composition of which sulphurous acid, peroxide of nitrogen, and water enter. As soon as this crystalline mass is treated with water, it is decomposed with brisk effervescence; $NO_4 + 2\,SO_2 + x HO$ yielding $NO_2 + 2\,(HO,SO_3) + x\text{-}2\,HO$; 1 atom of deutoxide of nitrogen escapes, and 2 atoms of sulphuric acid remain in solution: the deutoxide of nitrogen, by

again absorbing 2 atoms of oxygen from the air, is reconverted into peroxide of nitrogen; this combines again with two

FIG. 282.

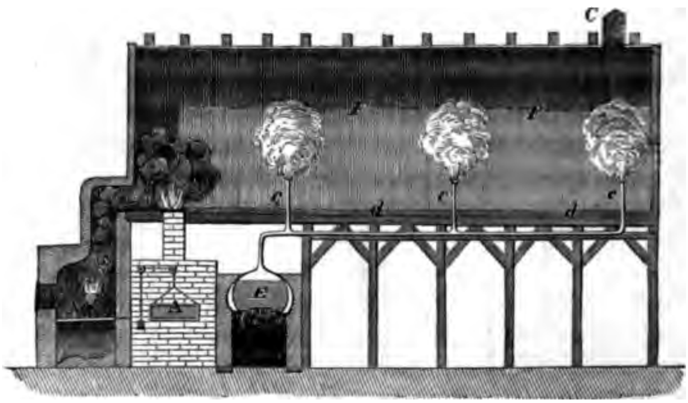


fresh atoms of sulphurous acid in the presence of a small quantity of water; fresh crystals are formed, and these in their turn are decomposed by solution, as before. The deutoxide of nitrogen is thus again liberated, and may go through the same round of compositions and decompositions, till the whole of the oxygen in the air has been consumed: the oxide of nitrogen thus acts the part of a carrier of oxygen to the sulphurous acid. In the manufacture of sulphuric acid on the large scale, the formation of the crystalline body and its destruction are simultaneous, if the operation be properly conducted,* so that no deposition of crystals actually occurs.

* The true composition of this crystalline body has been the object of much discussion and numerous experimental inquiries. H. Rose states that by passing pure dry deutoxide of nitrogen into a glass vessel, from which oxygen is carefully excluded, and the interior of which is moistened with anhydrous sulphuric acid $(SO_3)_2$, a white, hard, amorphous substance is formed; and this compound he regards as the essential constituent in the crystals above described. It fuses at a high temperature, and may be sublimed without decomposition. This substance Rose considered to have the composition NO_2, 2 SO_3; but Brüning has shown that during the formation of this compound sulphurous acid is liberated, in the proportion of 1 atom for each atom of deutoxide absorbed; and he found the crystalline compound to have a composition which may be represented by the formula NO_3, 2 SO_3. Water immediately decomposes it, liberating deutoxide of nitrogen, whilst the sulphuric

(345) In the manufacture of sulphuric acid, sulphurous acid is procured by burning either sulphur, or iron pyrites (FeS_2); provision being made for an abundant supply of atmospheric air to the burning material. The general arrangements adopted in the manufacture are shown in fig. 283. A, A, represent furnaces in

FIG. 283.



which the sulphur is burned: in the current of heated gas an iron pot, *b*, is suspended, which has been previously charged with a mixture of nitrate of soda and oil of vitriol. Vapours of nitric acid are thus liberated; they pass on with the sulphurous acid, by suitable flues, into immense chambers, F, F, constructed of sheet lead, and supported by a strong timber framework. These chambers are often 12 or 15 feet high, 15 or 20 wide, and from 150 to 300 feet in length; they are sometimes partially intersected by incomplete transverse leaden partitions, interposed in the current of the mixed gases, with a view of effecting their more intimate admixture. Water to the depth of 2 or 3 inches is placed upon the floor of the chamber, *d*, *d*, to condense the acid; and the mutual re-action of the atmospheric oxygen, sulphurous acid, and deutoxide

acid is dissolved. If the anhydrous crystals be exposed to the air, they absorb moisture and emit nitrous fumes. Concentrated oil of vitriol, by the aid of heat, dissolves them in all proportions without change; the solution crystallizes, on cooling, in rectangular prisms, which appear to contain water of crystallization.

Oil of vitriol rapidly absorbs deutoxide of nitrogen, and forms a crystalline compound similar to the foregoing; the addition of water immediately liberates the deutoxide of nitrogen from it.

There are many other methods by which this curious substance may be obtained, but they often involve very complicated considerations. De la Provostaye procures it by the action of liquid sulphurous acid on liquid peroxide of nitrogen; he considers it when anhydrous to consist of SO_2, SO_2, NO_4, which is consistent with the analysis of Brüning.

of nitrogen is further facilitated by the injection of steam at a pressure of about 10 lb. upon the inch by means of jets *c, c, c*, supplied from the boiler, E. The nitric acid extricated from the nitre speedily becomes deoxidized by the sulphurous acid to the state of deutoxide of nitrogen, and then the changes already pointed out rapidly succeed each other, and sulphuric acid is formed in large quantity.

In a properly managed chamber, the gases which pass off by the exit-flue, c, consist only of nitrogen and deutoxide of nitrogen, the sulphurous acid and oxygen being supplied in quantities just sufficient to effect their mutual condensation, fresh atmospheric air entering at the other end along with the sulphurous acid.

Gay-Lussac has taken advantage of the solubility of deutoxide of nitrogen in oil of vitriol, to economize the consumption of nitre in the process, which upon the old plan amounts to from one eighth to one twelfth of the weight of the sulphur consumed. By the contrivance to be mentioned immediately, the quantity of nitre formerly requisite has been reduced by one half, or even by two thirds. The improvement consists in conducting the spent gases into a leaden tower filled with fragments of coke, through which a stream of concentrated sulphuric acid is continually trickling. The acid thus becomes charged with the nitrous vapours, and flows off at the bottom of the tower to a reservoir from which it is again raised by a forcing pump to the top of a second similar tower at the entrance of the chamber, where it is deprived of the nitrous compounds by the sulphurous acid gas as it enters from the furnace. This plan has not as yet come into general use in this country.

The sulphuric acid which collects at the bottom of the chambers is in too dilute a condition for sale: it is not found advantageous to allow it to attain a greater degree of concentration than 1·60 in the chambers, since beyond this it becomes liable to absorb and retain the nitrous fumes.* When it has reached a specific gravity of about 1·60, it is sufficiently strong for the manufacture of salt-cake, but it requires concentration for other purposes: with this view it is drawn off and evaporated in shallow leaden pans till it has acquired a density of 1·720; beyond this point the concentration cannot be carried in these vessels, because the temperature required would endanger the melting of the leaden pan and its corrosion by the acid. This acid of sp. gr. 1·720 forms the *brown*

* The crude acid of sp. gr. 1·60 does not usually contain more than 0·6 per cent. of nitrous acid (Mr. Allhusen).

acid of commerce; it is extensively employed in the manufacture of superphosphate of lime for manures (1455), and for other coarse purposes. When required in a still more concentrated form, the brown acid is transferred into glass retorts, or, as is now practised in many works with great advantage, into platinum stills; in these it is again further heated until white fumes of oil of vitriol pass over. Beyond this point it is useless to carry the operation, as the concentrated acid distils over. Indeed during the whole operation some acid passes over with the water, which is therefore preserved, and returned to the leaden chamber.

The acid that remains in the retort after it has been thus boiled down, is the concentrated *oil of vitriol* of commerce; it is a definite hydrate of sulphuric acid, containing 1 atom of acid and 1 of water (HO, SO_3).*

The following table gives the proportion of sulphuric acid contained in solutions of the densities therein mentioned:—†

Strength of Sulphuric Acid of Different Densities at 60° F. (Ure).

Specific gravity.	SO_3 in 100 parts.	HO, SO_3.	Specific gravity.	SO_3 in 100 parts.	HO, SO_3.	Specific gravity.	SO_3 in 100 parts.	HO, SO_3.
1·8460	81·54	100	1·5503	53·82	66	1·2334	26·09	32
1·8415	79·90	98	1.5280	52·18	64	1·2184	24·46	30
1·8366	78·28	96	1·5066	50·55	62	1·2032	22·83	28
1·8288	76·65	94	1·4860	48·92	60	1·1876	21·20	26
1·8181	75·02	92	1·4660	47·29	58	1·1706	19·57	24
1·8070	73·39	90	1·4460	45·66	56	1·1549	17·94	22
1·7901	71·75	88	1·4265	44·03	54	1·1410	16·31	20
1·7728	70·12	86	1·4073	42·40	52	1·1246	14·68	18
1·7540	68·49	84	1·3884	40·77	50	1·1090	13·05	16
1·7315	66·86	82	1·3697	39·14	48	1·0953	11·41	14
1·7080	65·23	80	1·3530	37·51	46	1·0809	9·78	12
1·6860	63·60	78	1·3345	35·88	44	1·0682	8·15	10
1·6624	61·97	76	1·3165	34·25	42	1·0544	6·52	8
1·6415	60·34	74	1·2999	32·61	40	1·0405	4·89	6
1·6204	58·71	72	1·2826	30·98	38	1·0268	3·26	4
1·5975	57·08	70	1·2654	29·35	36	1·0140	1·63	2
1·5760	55·45	68	1·2490	27·72	34	1·0074	0·815	1

(346) *Protohydrate of Sulphuric Acid.*—The oil of vitriol of commerce forms a dense, oily looking, colourless liquid, without smell, and of specific gravity 1·842. It is intensely caustic, and chars almost all organic substances, from its powerful affinity for

* Marignac (*Ann. de Chimie*, III. xxxix. 189) finds that it always contains a slight excess of water beyond the atomic proportion; instead of 18·36 per cent. of water, he always obtained 19·62; and a similar observation was made by Gay-Lussac.

† Bineau has more recently made a careful determination of the strength of sulphuric acid of different densities (*Ann. de Chimie*, III. xxiv. 341), but

moisture. With water it mixes completely in all proportions, and the mixture, when cold, occupies less bulk than the two liquids did when separate. Great heat is given out at the moment the mixture is made; the dilution should therefore be performed gradually, always pouring the acid into the water, not the water into the acid. So powerful is the attraction of the acid for moisture, that if it be exposed in a shallow dish to the air for a few days, it frequently doubles its weight by absorbing aqueous vapour from the air. In the laboratory, advantage is frequently taken of this property, which enables it to be employed in a variety of cases as a desiccating agent (63 and 179). The acid of commerce is often of a dark brown colour, occasioned by its charring action on fragments of organic matter, such as straw or wood, which have accidentally fallen into it. Sulphuric acid does not evaporate at the ordinary temperature of the air. If a drop of the diluted acid fall upon a cloth, the water gradually evaporates until the acid which is left behind acquires a certain degree of concentration. On approaching a fire or other source of heat, a further portion of the water is expelled, and the acid becomes more concentrated, till it chars or destroys the cohesion of the fibres; this is one cause of the destructive action of sulphuric acid upon linen, even when very much diluted.

Marignac finds that the true protohydrate of sulphuric acid when heated emits a small quantity of the vapour of the anhydrous acid, and the remaining liquid boils at 640° F. Bineau states that just above the boiling point of the acid the vapour has a sp. gr. of 2·15, which would represent 2 volumes of the anhydride and 2 volumes of steam (1 equivalent of each) condensed into the space of 3 volumes, but it continues to expand by heat until at 880° an equivalent of the hydrate occupies the space of 4 volumes, which would reduce the density of the vapour to 1·692. After the acid has been frozen, it melts at 51°, but it may be cooled much below this point without solidifying. On dropping into the cooled acid a

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his results differ but slightly from those of Ure, as may be seen from the annexed table (temp. 59° F.):—

Specific gravity.	HO, SO_3 in 100 parts.	Specific gravity.	HO, SO_3 in 100 parts.	Specific gravity.	HO, SO_3 in 100 parts.
1·842	100	1·501	60	1·144	20
1·822	90	1·398	50	1·068	10
1·734	80	1·306	40	1·032	5
1·615	70	1·223	30		

crystal of the acid previously frozen, congelation immediately occurs, and the temperature rises to 51°. The concentrated acid of commerce does not usually freeze till it has been cooled to about—30°; but it does not become liquid till the temperature reaches 32°.

Second Hydrate of Sulphuric Acid ($HO, SO_3 + HO$).—If water be added to sulphuric acid, until the density is reduced to 1·78, a second hydrate, which contains 2 atoms of water, is formed. It freezes at 47°, and crystallizes in splendid rhombic prisms, the sp. gr. of which is 1·951; from this property it is often termed *glacial sulphuric acid*. According to Dalton, it boils at 435°. Graham found that this hydrate may be obtained by heating a more diluted acid to 400° till it ceases to give off water.

A *third hydrate* ($HO, SO_3 + 2\ HO$) may, according to Graham, be procured by evaporating a dilute acid *in vacuo* at 212°, till it ceases to lose weight. The density of this hydrate is 1·632, and its boiling point is 348°.

Nordhausen Sulphuric Acid.—For the purpose of dissolving indigo in the process of dyeing Saxony blue, an acid of still higher concentration than oil of vitriol is required. Such an acid is principally prepared at the town of Nordhausen, in Saxony, and is hence known as *Nordhausen oil of vitriol*. The old name for sulphate of iron was *green vitriol*, and this circumstance, taken in conjunction with the oily consistence of the concentrated acid, gave rise to the name of *oil of vitriol*, by which the monohydrated acid is still frequently known, and which is convenient as distinguishing it from more diluted acids. In preparing it, sulphate of iron is dried at a moderate heat to expel its water of crystallization, and is then distilled in earthen retorts; a dense, brown, fuming liquid passes over, of sp. gr. about 1·9.

Sulphuric Anhydride $(SO_3)_2$.—If this fuming Nordhausen acid be placed in a glass retort, furnished with a receiver which is kept cool by ice, and a gentle heat be applied to the retort, white fumes pass over, which solidify into a white, silky-looking, fibrous mass. This is the compound of 2 atoms of sulphur with 6 of oxygen, commonly called *anhydrous sulphuric acid*. The remainder in the retort, after all the anhydride is expelled, consists of ordinary oil of vitriol. Sulphuric anhydride may also be obtained from the acid sulphate of soda ($NaO, HO, 2\ SO_3$), which melts at a dull red heat, and is deprived of its atom of water; after which, if distilled in an earthen retort, it yields white fumes of the anhydride, whilst neutral sulphate of soda (NaO, SO_3) remains in the retort. The anhydride forms with 2 atoms of oil of vitriol a compound that crystallizes in plates consisting of $HO, 2\ SO_3$, which fuse at 95°.

The so-called anhydrous sulphuric acid, however, possesses no acid properties. It is tough, ductile, and can be moulded in the fingers, like wax, without charring the skin. It fumes in the air, and is very deliquescent; when thrown into water the heat emitted is so intense that it hisses as a hot iron would do. The solution has all the properties of ordinary sulphuric acid. The anhydride melts at 65°, and boils at about 110°, forming a colourless vapour, which if passed through ignited porcelain tubes is decomposed into 4 volumes of sulphurous acid and 2 of oxygen; 2 volumes of sulphur vapour and 6 of oxygen being condensed in the anhydride into the space of 4 volumes of vapour. The specific gravity of this vapour was found by Mitscherlich to be 3·01, or somewhat higher than its calculated amount, which is 2·764: for—

			By weight.		By volume.			Sp. gr.
Sulphur	S_2	=	32	or 40	2	or 0·5	=	1·1056
Oxygen	O_6	=	48	60	6	1·5	=	1·6584
Sulphuric Anhydride	S_2O_6	=	80	100	4	1	=	2·7640

According to Marignac, sulphuric anhydride exists under two modifications; one of which melts at about 65°, and is produced by distillation, or by fusion at a high temperature; but when once it has been solidified, it passes rapidly into the other form, which melts near 212°, at which temperature it is slowly volatilized, and becomes reconverted into the first variety.

Sulphuric anhydride combines with sulphur, forming solutions which have a brown, green, or blue colour, according to the proportion of sulphur; the blue compound containing the smallest proportion. It likewise dissolves iodine, and with one-tenth of its weight of iodine forms a green crystalline compound. It also combines with hydrochloric acid, and forms a liquid termed *chlorhydrosulphuric* acid (HCl, S_2O_6), which boils at 293°.

We are therefore acquainted with the following definite compounds of sulphuric acid with water; starting with the anhydride :—

Hydrate.	Formula.	Fusing point, °F.	Boiling point, °F.	Specific gravity.
Sulphuric anhydride .	$(SO_3)_2$	65		
Dihydrate	$HO, (SO_3)_2$	95		
Monohydrate . . .	HO, SO_3	51	640	1·842
Bihydrate	$HO, SO_3 + HO$	47	435	1·780
Terhydrate	$HO, SO_3 + 2\ HO$		348	1·632

Uses.—The applications of sulphuric acid in the arts are very numerous. Immense quantities of it are consumed in the manu-

facture of sulphate of soda as a preliminary process in making carbonate of soda; and it is in constant requisition for the preparation of nitric, hydrochloric, and other volatile acids. Its applications in the laboratory are too numerous to be specified.

(347) *Impurities common in the Commercial Acid.*—The oil of vitriol of commerce is never pure: it always contains lead, derived from the vessels in which it is made. The greater part of the sulphate of lead is precipitated as a white powder when the acid is diluted. It is also frequently contaminated with arsenic, derived from the pyrites: the diluted acid in this case gives a yellow precipitate when exposed to a current of sulphuretted hydrogen gas. The arsenic is still more easily recognised by what is termed Marsh's test, which will be described under the head of arsenic (709). On the large scale this impurity is effectually removed by adding a small quantity of sulphide of barium to the acid: sulphide of arsenic and sulphate of baryta are formed; they are both insoluble in the acid, and may be separated by subsidence and decantation. It may also be got rid of by adding hydrochloric acid and boiling the liquid, when the arsenic is expelled in the form of chloride of arsenic with the excess of hydrochloric acid. Nitric acid and some of the lower oxides of nitrogen are also often present: a strong solution of green vitriol in water, when added to the undiluted acid, shows the presence of these impurities by striking a characteristic purplish-red colour at the point of contact of the two liquids. Sulphurous acid may likewise sometimes be detected in the acid, as may also hydrochloric acid and sulphate of potash.

When required in a pure form, the acid must be re-distilled with a little sulphate of ammonia; this salt decomposes any nitrous acid which may be present (p. 102). The distillation requires to be conducted with much care, as the boiling takes place with violent concussions and sudden bursts of vapour: the danger may be avoided by distilling it from broken crystals of quartz; or by using a gas-burner in the form of a large ring, so as to apply heat to the sides, and not to the bottom of the retort, in which case the insoluble matters collect at the bottom of the retort, whilst the ebullition takes place from the sides tranquilly.

Sulphuric acid in its concentrated form acts but feebly upon metallic bodies in the cold, but when boiled upon them it in some cases undergoes decomposition: even silver is dissolved by it; the metal is oxidized at the expense of part of the oxygen of the acid, sulphurous acid being formed, whilst the sulphate of the metal is dissolved in the excess of sulphuric acid; thus $Ag + 2\,(HO, SO_3)$ become $AgO,SO_3 + SO_2 + 2\,HO$. Copper, mercury, arsenic, anti-

mony, bismuth, tin, lead, and tellurium are acted upon by the acid in a similar manner. Gold, platinum, rhodium, and iridium are not acted upon by the acid even when boiled with it. The more oxidizable metals are dissolved by this acid when diluted with water, water being decomposed and hydrogen liberated, whilst the oxygen of the water combines with the metal, and the metallic oxide at the moment of its formation unites with the sulphuric acid: zinc, iron, cobalt, nickel, and manganese are acted upon in this way. The acid is also decomposed when boiled with charcoal or with sulphur, sulphurous acid being evolved.

Sulphates.—The salts formed by sulphuric acid are termed *sulphates;* they are for the most part composed of 1 equivalent of acid and 1 of metallic oxide, like sulphate of zinc ($ZnO,SO_3 + 7\ HO$). There are, however, strong grounds for believing that sulphuric acid is what is termed a dibasic acid (460). Its ordinary formula would in this case require to be doubled, and would be written $2\ HO,\ S_2O_6$: neutral sulphate of zinc being $2\ ZnO,\ S_2O_6 + 14\ Aq$. With the alkalies it forms acid salts, such as bisulphate of potash ($KO,HO,2\ SO_3$): in a few instances basic salts, such as the subsulphate of copper ($3\ CuO,SO_3 + 2\ Aq$), may be formed. The soluble sulphates of the metallic oxides may be readily prepared by dissolving the oxide or its carbonate in diluted sulphuric acid, in cases in which the metal itself is not readily attacked by the acid. The insoluble sulphates, such as those of baryta and lead, may be obtained by precipitating a soluble salt of the base by means of some soluble sulphate, such as sulphate of soda. Many of the sulphates are formed as residues during the preparation of the volatile acids by the action of sulphuric acid on their salts. Sulphate of potash is thus obtained during the preparation of nitric acid from saltpetre, sulphate of soda as a residue from common salt in the manufacture of hydrochloric acid, and so on. The sulphates of potash, baryta, strontia, lead, silver, and of both the oxides of mercury, are anhydrous. Sulphate of lime (gypsum) contains $CaO,SO_3 + 2\ Aq$. The sulphates of zinc, magnesia, and of the protoxides of iron, cobalt, and nickel, usually crystallize with 7 Aq; but the number of atoms of water in these salts is often smaller if the solution is allowed to crystallize at a high temperature, the proportion of water being sometimes 5 Aq, at others 4 Aq, and under some circumstances as low as 2 Aq. The sulphates of this group (which are isomorphous with sulphate of magnesia) contain 1 atom of water, which admits of displacement by an atom of some anhydrous sulphate, such as sulphate of potash, or sulphate of ammonium ($H_4NO,\ SO_3$):

peculiar double salts are thus formed, which retain 6 atoms of water of crystallization, but these double salts are still isomorphous with sulphate of magnesia (461). Sulphate of copper crystallizes with 5 Aq, but it forms double salts containing 6 Aq, such as (CuO,SO_3. KO,SO_3+6Aq) isomorphous with those just mentioned. Sulphate of soda crystallizes usually as (NaO,SO_3+10 Aq), but it exhibits some singular anomalies (488).

The sulphates of the alkalies and of the alkaline earths are not decomposed when heated to redness, except the sulphate of magnesia, which loses its acid partially; the sulphates of zinc, cadmium, nickel, cobalt, copper, and silver require an intense heat to decompose them; but the other sulphates part with their acid without difficulty when strongly ignited. When heated with charcoal the sulphates are all decomposed; those of the alkalies and alkaline earths being converted into sulphides: these sulphides, when moistened with hydrochloric acid, evolve sulphuretted hydrogen. The sulphate of baryta may be easily recognised, even in small quantity, if, after having been mixed with a little charcoal and folded in a piece of platinum foil, it is heated in the flame of the blowpipe; $BaO,SO_3+4\,C$ become $BaS+4\,CO$; the carbonic oxide escaping as gas; and the sulphide of barium, when moistened with hydrochloric acid, is converted into chloride, and evolves hydrosulphuric acid; $BaS+HCl=BaCl+HS$. The sulphates of the alkalies and alkaline earths may also be converted into sulphides by heating them to redness in a glass or porcelain tube, and transmitting a current of dry hydrogen gas over them. In this way sulphate of potash is reduced without difficulty to sulphide of potassium, water being formed; $KO,SO_3+4\,H$ yielding $KS+4\,HO$.

Sulphuric acid and its salts are easily recognised when in solution by the white precipitate of sulphate of baryta which is formed on the addition of nitrate of baryta; this precipitate is very nearly insoluble in nitric acid. A white precipitate of sulphate of lead, nearly as insoluble as the sulphate of baryta, is formed on adding a soluble salt of lead to a solution containing sulphuric acid or a sulphate. The sulphates of strontia, lime, and silver are but sparingly soluble in water; the others are readily soluble; nearly all the sulphates are insoluble in alcohol, unless a large excess of acid be present. The sulphates which are insoluble in water and in acids may be entirely decomposed by fusion with an excess of carbonate of soda or potash, a sulphate of the alkali being formed, which may be dissolved by water, whilst an insoluble carbonate of the base is left. A solution of the carbo-

nates of the fixed alkalies, when boiled with the insoluble sulphates, produces a similar but less complete decomposition.

(348) Hyposulphurous Acid, not isolated ($HO, S_2O_2 = 9 + 148$).—Of the remaining acids of sulphur, the only one of any practical importance is the hyposulphurous or *dithionous* acid. In combination with soda it has been largely employed in the fixing of photographic pictures. This application has arisen from the power possessed by this compound of dissolving those salts of silver which are insoluble in water, forming with them soluble double salts; the surface of the photograph is freed from the unaltered argentine compound by immersion in a solution of the hyposulphite, whilst the portion which has been blackened by light is left unacted upon; if, after this operation, the picture be well washed with water, it is no longer liable to alteration by exposure to light.

If zinc filings be digested in a solution of sulphurous acid, the metal is dissolved without any extrication of gas; it is oxidized at the expense of a portion of the sulphurous acid, and a mixture of sulphite and hyposulphite of zinc is found in solution; $3 SO_2 + 2 Zn$ becoming $ZnO, S_2O_2 + ZnO, SO_2$.

Hyposulphite of Soda ($NaO, S_2O_2 + 5 Aq$) is manufactured to some extent by transmitting through a solution of impure sulphide of sodium (prepared by fusing together in a covered crucible equal weights of carbonate of soda and flowers of sulphur) a stream of sulphurous acid until it ceases to be absorbed; the liquid is then filtered and evaporated; hyposulphite of soda crystallizes from the solution in bold striated rhombic prisms, terminated by oblique faces. A still better plan consists in digesting a solution of sulphite of soda on powdered sulphur: the sulphur is gradually dissolved and forms a colourless solution, which on evaporation yields crystals of hyposulphite of soda, 1 atom of sulphur combining with 1 atom of sulphite of soda; $NaO, SO_2 + S$ becoming NaO, S_2O_2. When heated in closed vessels the hyposulphite of soda first loses water, and is then resolved into sulphate of soda and pentasulphide of sodium; $4 (NaO, S_2O_2) = 3 (NaO, SO_3) + NaS_5$. The *hyposulphites of lime* ($CaO, S_2O_2 + 6 Aq$) and *strontia* ($SrO, S_2O_2 + 5 Aq$) may be prepared by transmitting sulphurous acid through a solution of the sulphides of calcium and strontium; their solutions are decomposed below the temperature of 212° into free sulphur and sulphites of the earths.

Hyposulphite of Baryta ($BaO, S_2O_2 + Aq$) may be obtained in small brilliant crystals by mixing dilute solutions of chloride of barium and hyposulphite of soda. It is impossible, however, to obtain the acid in the form of a hydrate either from this or from

any of its salts; when, for example, sulphuric acid is added to the hyposulphite of baryta, sulphate of baryta is precipitated, but if the solution be filtered, the clear liquid speedily becomes milky from the separation of sulphur, and the odour of sulphurous acid is emitted; HO,S_2O_2 becoming decomposed into $S+SO_2+HO$.

Rose states that none of the hyposulphites can be obtained in the anhydrous form, all of them retaining at least 1 atom of water, which cannot be expelled without completely decomposing the salt, so that probably their true formula should be MO, S_2HO_3; that of the baryta salt, for instance, instead of being BaO, S_2O_2+Aq, should be BaO, S_2HO_3.

The soluble hyposulphites are easily recognised by the facility with which they dissolve chloride of silver, forming a solution of an intensely sweet taste; $AgCl+2\ (NaO, S_2O_2)=NaCl+NaO, AgO, 2\ S_2O_2$. Solutions of the hyposulphites give a white precipitate of hyposulphite of lead in solutions of the salts of lead; this precipitate, however, becomes decomposed and blackened if dried at 212°, owing to its partial conversion into sulphide of lead: a solution of nitrate of suboxide of mercury is immediately decomposed by a solution of the hyposulphites at ordinary temperatures in a similar manner, the black sulphide of mercury being deposited. These salts also give a brown precipitate, consisting of sulphide of copper, when heated with a solution of a salt of copper acidulated with hydrochloric acid. An alcoholic solution of iodine is rendered colourless by admixture with an excess of hyposulphite, a tetrathionate of the base being produced (351).

The *Hyposulphite of Gold and Soda* [$AuO, S_2O_2.\ 3\ (NaO, S_2O_2)+4\ Aq$] is used for gilding the daguerreotype plate and for colouring the positive proof obtained in photographic printing. It may be prepared in a state of purity, by mixing concentrated solutions of 1 part of chloride of gold and 3 parts of hyposulphite of soda; chloride of sodium, tetrathionate of soda, and hyposulphite of soda and gold being formed: on the addition of alcohol the latter salt is precipitated; the precipitate must be redissolved in a small quantity of water, and again precipitated by alcohol. It crystallizes in groups of colourless needles, which are very soluble in water, but insoluble in alcohol. It may be mixed with diluted sulphuric or hydrochloric acid without the evolution of sulphurous acid.

The formation of this double salt is explained by the following equation (Fordos and Gélis, *Ann. de Chimie*, III. xiii. 399):—

$$8\overbrace{(NaO,\ S_2O_2)}^{\text{Hyposulph. soda.}}+\overbrace{AuCl_3}^{\text{Chlor. gold.}}=2\overbrace{(NaO,\ S_4O_5)}^{\text{Tetrathion. soda.}}+\overbrace{AuO,\ S_2O_2,\ 3\,(NaO,\ S_2O_2)}^{\text{Hyposulphite soda and gold.}}+3\overbrace{NaCl}^{\text{Chlor. sodium.}}$$

(349) Hyposulphuric Acid: *Dithionic Acid* ($HO,\ S_2O_5=9+72$).—This acid is more stable than the hyposulphurous acid, and may be obtained in combination with water. If sulphurous acid gas be transmitted through water in which finely divided peroxide of manganese is suspended, the gas is rapidly absorbed, and if the liquid be kept cool, hyposulphate of manganese is formed; $MnO_2+2\ SO_2$ yielding $MnO,\ S_2O_5$. If the temperature be allowed to rise, sulphate of manganese is formed instead; MnO_2+SO_2 becoming $MnO,\ SO_3$. It is difficult to prevent the formation of a little of the latter salt, but the two salts are easily separated; by adding baryta water the protoxide of manganese is precipitated, and sulphate and hyposulphate of baryta are formed; $MnO,\ SO_3+MnO,\ S_2O_5+2\ (BaO, HO)=BaO,\ SO_3+BaO,\ S_2O_5+2\ (MnO,\ HO)$. The hyposulphate of baryta, being soluble, may be separated from the insoluble sulphate of baryta by filtration, and it may be obtained in prismatic crystals ($BaO,\ S_2O_5+4\ Aq$) by evaporation: by the cautious addition of diluted sulphuric acid to its solution, until a precipitate ceases to be formed on the addition of a drop of sulphuric acid, hyposulphuric acid may be liberated and filtered from the sulphate of baryta.

The hyposulphates are all soluble in water. The solid salts when heated emit sulphurous acid, whilst a sulphate of the base remains behind. When in solution they may be oxidized at a boiling heat by chlorine or by nitric acid, and two atoms of sulphuric acid are formed; $S_2O_5+O=2\ SO_3$. In the cold, they present no appearance of decomposition when treated with sulphuric acid, but if heated with it, sulphurous acid is evolved, but no deposit of sulphur occurs. These reactions distinguish the hyposulphates from both the sulphites and hyposulphites.

(350) Trithionic Acid, ($HO,\ S_3O_5=9+88$).—If a saturated solution of bisulphite of potash be digested on flowers of sulphur for three or four days, till the yellow colour has disappeared, sulphurous acid gradually escapes and trithionate of potash is formed. It crystallizes in anhydrous four-sided prisms, terminated by dihedral summits. A solution of the salt gives a black precipitate with subnitrate of mercury, and a white with the pernitrate of mercury; with nitrate of silver it gives a yellowish white precipitate, which soon becomes black. The trithionate of potash may be decomposed by means of tartaric acid, and the liberated trithionic

acid has even been obtained in prismatic crystals, but its solution gradually undergoes spontaneous decomposition into sulphur and sulphurous and sulphuric acids; $HO, S_3O_5 = S + SO_2 + HO, SO_3$. When the trithionates are heated in a closed tube, sulphur is sublimed, sulphurous acid is expelled, and sulphate of the base is left.

(351) Tetrathionic Acid ($HO, S_4O_5 = 9 + 104$).—When hyposulphite of baryta is suspended in water, and iodine is added, iodide of barium is formed, and a new, sparingly soluble salt, the tetrathionate of baryta, is separated in hydrated crystals:—

$$2\,(BaO, S_2O_2) + I = BaI + BaO, S_4O_5.$$

The tetrathionate is purified by recrystallization; and from a solution of this salt a pure solution of tetrathionic acid may be prepared by the addition of a quantity of sulphuric acid just sufficient to precipitate the whole of the baryta; the acid may be concentrated *in vacuo* over sulphuric acid. By boiling the solution, sulphur is deposited, sulphurous acid escapes, and sulphuric acid remains in the liquid.

(352) Pentathionic Acid ($HO, S_5O_5 = 9 + 120$).—A solution of sulphurous acid is decomposed by transmitting through it a current of sulphuretted hydrogen; sulphur is deposited, and a new acid remains in the liquid; $5\,SO_2 + 5\,HS$ yielding $HO, S_5O_5 + 5\,S + 4\,HO$. It is very unstable: tetrathionic and trithionic acids are formed in the solution, attended with a deposition of sulphur. The *pentathionate of baryta* ($BaO, S_5O_5 + Aq$) may be obtained in silky scales by neutralizing the acid with baryta water, and precipitating the salt from its aqueous solution by the addition of alcohol: subnitrate of mercury gives a yellow precipitate in its solution; and nitrate of silver a yellow precipitate, which quickly becomes decomposed and turns black.

The action of sulphuric acid upon the salts of the various oxy-acids of sulphur, affords a valuable means of distinguishing between several of these different classes of salts. When concentrated sulphuric acid is poured upon the sulphates, it evolves no odour, even when heated with them. The sulphites, even in the cold, yield, with diluted sulphuric acid, an odour of sulphurous acid. The hyposulphates emit no odour of sulphurous acid with diluted sulphuric acid in the cold, but evolve sulphurous acid by the aid of heat: whilst diluted sulphuric acid produces with the hyposulphites, even in the cold, an odour of sulphurous acid attended with a deposit of sulphur.

(353) Chlorosulphuric Acid, *Chloride of Sulphuryl* $(SO_2Cl)_2$; *Sp. Gr. of Liquid*, 1·66; *of Vapour*, 4·703; *Boiling Pt.* 170°; *Comb. Vol.* 4.—If equal measures of sulphurous acid and of chlorine, both perfectly dry, be mixed together, no change occurs in diffused daylight, but under the influence of bright sunshine they unite and become condensed into a colourless liquid, with an extremely pungent odour, and an irritating effect upon the eyes.* This substance can scarcely be called an acid, for it does not form any peculiar class of salts. It may be distilled unchanged from caustic lime or baryta; but by admixture with water it is immediately decomposed into sulphuric and hydrochloric acids; $(SO_2Cl)_2 + 4\ HO$ yielding $2\ (HO,\ SO_3) + 2\ HCl$. An analogous compound may be formed with iodine. These bodies are considered by H. Rose and by Berzelius, as compounds of sulphuric acid with chloride or iodide of sulphur; $3\ SO_2Cl = 2\ SO_3,\ SCl_3$. Rose has obtained a fuming oily-looking compound, which boils at 293° F., containing SO_3, SO_2Cl, which both Rose and Berzelius regard as $(5\ SO_3,\ SCl_3)$. It should be stated, in opposition to this view of Berzelius, that no compound of chlorine, SCl_3, is known to exist, and the density of the vapour of chloride of sulphuryl is in favour of the simpler formula.

(354) Nitrosulphuric Acid $(HO,\ SO_2NO_2 = 9 + 62)$; not known, uncombined with bases.—Deutoxide of nitrogen and sulphurous acid may be mixed with each other in a dry state without entering into combination, but if a strong solution of potash be thrown up into a jar containing a mixture of 2 volumes of the deutoxide and 1 volume of sulphurous acid, over mercury, the gas is gradually and completely absorbed. If a concentrated solution of ammonia be saturated with sulphurous acid, then mixed with four or five times its bulk of the solution of ammonia, and a current of deutoxide of nitrogen be slowly transmitted, whilst the liquid is artificially kept cool, the gas is in great measure absorbed, and beautiful snow-white crystals of nitrosulphate of ammonia $(H_4NO,\ SO_2NO_2)$ are deposited; they may be collected on a filter, washed with a little ice-cold solution of ammonia, and dried *in vacuo* over sulphuric acid.

This salt is a singularly unstable compound; when dissolved in water it begins to undergo decomposition at ordinary tempera-

* It may be obtained more easily by distilling an intimate mixture of pentachloride or of oxychloride of phosphorus with sulphate of lead, phosphate of lead and chloride of sulphuryl being formed (Carius); the reaction with the oxychloride being as follows:—

$$6\ (PbO,\ SO_3) + 2\ PO_2Cl_3 = 2\ (3PbO,\ PO_5) + 3\ (SO_2Cl)_2.$$

tures: the presence of a free alkali increases its stability. If an attempt be made to liberate the acid by the addition of another acid to the salt, brisk effervescence, due to the escape of protoxide of nitrogen, takes place, and sulphuric acid remains in the liquid, HO,SO_2NO_2 giving $HO,SO_3 + NO$. Mere admixture of the solution of the nitrosulphate of ammonia with that of many metallic salts, such for instance as sulphate of copper, produces a similar decomposition: probably a double decomposition occurs; $CuO, SO_3 + H_4NO, SO_2NO_2$ becoming $CuO, SO_2NO_2 + H_4NO, SO_3$; the nitrosulphate of copper being immediately resolved into protoxide of nitrogen and sulphate of copper. If the dry nitrosulphate of ammonia be heated a little above 230°, it is decomposed with explosive evolution of the protoxide of nitrogen.

The nitrosulphates of potash and soda are rather more stable. No insoluble nitrosulphates have been formed; they give no precipitate with baryta water. The nitrosulphates of the alkalies are neutral to test paper, and have a pungent bitterish taste.

(354 *a*) *Compounds of Sulphurous and Nitrous Acids; Sulphazotised Acids of Fremy.*—A remarkable series of salts has been described by Fremy (*Ann. de Chimie*, III. xv. 408), formed by the action of sulphurous acid upon nitrite of potash containing a large excess of free alkali. Sulphurous acid combines with the elements of nitrite of potash and water in several different proportions, and forms compounds which crystallize readily, and in which neither sulphurous nor nitrous acid can be detected by the usual tests. The solutions of these salts produce, in solutions of salts of baryta, a precipitate which contains the new acid. These compounds are all decomposed by boiling their solutions, and ammonia and sulphuric acid are amongst the products; and some of them even experience a similar decomposition at ordinary temperatures.

The subjoined formulæ will sufficiently indicate the derivation of these salts from nitrite of potash, water, and sulphurous acid:—

Sulphazite of potash,	$3\,KO, S_3NH_3O_{12}$	or	$3\,KO, NO_3 + 3\,SO_2 + 3\,HO$
Sulphazate of potash,	$3\,KO, S_4NH_3O_{14}$	or	$3\,KO, NO_3 + 4\,SO_2 + 3\,HO$
Sulphazotate of potash,	$3\,KO, S_5NH_3O_{16}$	or	$3\,KO, NO_3 + 5\,SO_2 + 3\,HO$
Sulphammonate of potash,	$4\,KO, S_8NH_3O_{22}$	or	$4\,KO, NO_3 + 8\,SO_2 + 3\,HO$

It is remarkable that if nitrite of soda be substituted for nitrite of potash, no sulphazotised salts are formed. Indeed, Fremy was unable to procure any such compound which contained soda.

The sulphammonate of potash is easily formed by mixing a strong solution of sulphite of potash with one of nitrite of potash; the sulphammonate is deposited in beautiful silky needles.

Compounds of Sulphur with Hydrogen.

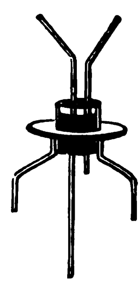
(355) Hydrosulphuric Acid: *Sulphuretted Hydrogen* ($HS = 17$). *Comb. Vol.* 2; *Sp. Gr.* 1·1912.—Sulphur forms with hydrogen an important compound commonly termed sulphuretted hydrogen, but which, as it possesses feebly acid properties, may be more fitly called hydrosulphuric acid. It is formed in small quantities when sulphur is heated in hydrogen gas, but it is always prepared for use by decomposing one of the metallic sulphides with an acid.

Preparation.—1. For ordinary purposes, about half an ounce of sulphide of iron (FeS), in small fragments, is placed in a bottle, and is decomposed in the cold by an ounce of sulphuric acid diluted with 6 or 8 times its bulk of water; gas is immediately formed in abundance: the oxygen of the water enters into combination with the iron, forming oxide of iron, which is dissolved by the acid, while the hydrogen takes up the sulphur and escapes; $FeS + HO, SO_3$ becoming $HS + FeO, SO_3$.

The gas which is procured in this manner is commonly contaminated with free hydrogen, because the sulphide of iron often contains a portion of metallic iron disseminated through it. Fig. 284 shows a convenient method of mounting an apparatus for dis-

Fig. 284.

Fig. 285.



engaging a continuous current of the gas from sulphide of iron. The cork through which the tubes pass is not fitted at once into the bottle, B or C, but is made to fit, as at *a*, into a piece of stout glass tube, open at both ends, such as is shown in fig. 285; this tube is ground so as to close the neck of the bottle air tight, like an ordinary stopper. The apparatus, which requires to be frequently dismounted in order to be charged afresh, may thus be

kept in a serviceable condition without the trouble or loss of time consequent on the frequent renewal of the corks, which would be needed unless this expedient were adopted. The various small tubes are connected together by long pieces of vulcanized caoutchouc tubing.

2.—When the gas is required in a state of purity, 1 part of powdered sulphide of antimony is substituted for the sulphide of iron: in this case it is necessary to employ 3 or 4 parts of hydrochloric acid of sp. gr. 1·1, and to apply a gentle heat to the mixture; the apparatus may then be arranged as in fig. 286. In either case the gas requires to be washed before collecting it, in order to remove any particles of the acid or of the metal which may have been carried over with it in mechanical suspension. As the compound of antimony with sulphur is a tersulphide (SbS_3), 1 atom of it requires 3 atoms of hydrochloric acid for its decomposition, and furnishes 1 atom of terchloride of antimony and 3 atoms of sulphuretted hydrogen: $SbS_3 + 3\,HCl$ yielding $SbCl_3 + 3\,HS$.

FIG. 286.

Properties.—Hydrosulphuric acid is a transparent colourless gas, of a disgusting odour, resembling that of rotten eggs. It is highly poisonous when respired in a concentrated form, and even when diluted with from 600 to 1200 times its bulk of air, is rapidly fatal to the lower animals. It is inflammable, and burns with a pale, bluish flame, depositing sulphur if the supply of air be insufficient for complete combustion. If transmitted through tubes heated to full redness, it is partially decomposed into sulphur and free hydrogen. Its density a little exceeds that of atmospheric air, 100 cubic inches weighing rather more than 38 grains.

Composition.—The proportion of hydrogen in a given volume of the gas may be ascertained by heating some granulated tin in a small retort filled with sulphuretted hydrogen and inverted in a vessel of mercury: the sulphur combines with the tin, whilst the hydrogen which remains occupies when cold the same space as the

gas before it was decomposed. Potassium cannot be employed instead of tin in this case, because, though it decomposes the gas, the sulphide of potassium which is formed enters into combination with another portion of the gas without decomposing it. In sulphuretted hydrogen, 1 volume of sulphur vapour and 2 volumes of hydrogen are therefore condensed into the space of two volumes, and the composition of the gas may be thus represented:—

		By weight.		By vol.	Sp. gr.
Sulphur	S = 16	or 94·12	2	or 1·0	= 0·069
Hydrogen	H = 1	5·88	1	0·5	= 1·105
	HS = 17	100·00	2	1·0	1·174

Sulphurous acid and sulphuretted hydrogen, in the presence of moisture, decompose each other, half the oxygen of the sulphurous acid uniting with the hydrogen of the sulphuretted hydrogen, water and pentathionic acid (352) being formed, whilst sulphur is deposited. For complete decomposition, 2 volumes of sulphuretted hydrogen and 1 volume of sulphurous acid would be requisite; $5\ SO_2 + 5HS = 5\ S + 5\ HO + S_5O_5$. A large proportion of the sulphur thus deposited is in the electropositive form (341*a*), and is insoluble in bisulphide of carbon.

Hydrosulphuric acid is also immediately decomposed by chlorine, bromine, and iodine; sulphur being precipitated, and hydrochloric, hydrobromic, or hydriodic acid being formed by the hydrogen, which combines with one or other of the elements above mentioned.

Under a pressure of about 17 atmospheres, sulphuretted hydrogen is reducible to a colourless, extremely mobile liquid, which freezes to a transparent mass at a temperature of —122°.

Water at 32° dissolves 4·37 times its bulk of sulphuretted hydrogen; 3·23 times its bulk at 59°, and 2·66 at 75° (Bunsen). The solution is feebly acid, and has the smell and taste of the gas. When exposed to the air, this solution becomes milky; the hydrogen is slowly oxidized, forming water, and the sulphur is separated. If the oxidation of sulphuretted hydrogen take place in a moist atmosphere, a little sulphuric acid is formed, and this action is favoured by the presence of a base to combine with the newly-formed acid.

Sulphuretted hydrogen is formed spontaneously under a variety of circumstances. Whenever a soluble sulphate remains in contact with decaying animal or vegetable matter, the sulphate loses oxygen, which combines with the elements of the decaying substance, whilst sulphide of the metal remains: sulphate of lime,

for example, by the abstraction of 4 atoms of oxygen, becomes converted into sulphide of calcium; thus, $CaO,SO_3-O_4=CaS$.

In this way soluble sulphides are formed in many springs, such as those of Harrogate, giving to them their peculiar sulphureous odour; and, in a somewhat similar manner, sulphuretted hydrogen is generated in large quantities in stagnant sewers and cesspools.

The sulphides thus formed are readily decomposed by acids,—even the carbonic acid contained in the atmosphere being sufficient to cause the expulsion of sulphuretted hydrogen, and thus to occasion the odour observed on exposing such compounds to a damp air.

(356) *Hydrosulphates, or Sulphides.*—Hydrosulphuric acid, though a feeble acid, combines readily with bases: for example, if the gas be transmitted into a solution of potash or solution of ammonia, it is rapidly absorbed, hydrosulphate of potash, KO, HS, or hydrosulphate of ammonia, H_3N, HS, being formed. Such solutions are, however, generally regarded as sulphides of the metals, because the hydrogen of the acid is exactly equivalent to the oxygen of the base, and is capable, as in the analogous case of the chlorides, of forming water and a metallic sulphide: for example, hydrosulphate of potash (KO, HS) may be regarded as sulphide of potassium and water, or as $KS+HO$. Moreover, the action of sulphuretted hydrogen in cases in which it occasions a precipitate in the solution of a metallic salt, consists in the formation of an insoluble metallic sulphide: when, for instance, sulphate of copper in solution is treated with sulphuretted hydrogen, an abundant black precipitate of sulphide of copper is produced, water is formed, and the liquid becomes acid from the liberation of sulphuric acid; CuO, SO_3+HS, becoming HO, SO_3+CuS. A large number of the metallic sulphides when thus formed combine, it is true, with water at the moment of their precipitation.

Sulphuretted hydrogen is in continual requisition in the laboratory as a test for the discovery of metallic bodies: it gives characteristic precipitates with many metallic salts; for instance, with the compounds of lead it gives a black, with those of arsenic a yellow, and with those of antimony an orange-coloured precipitate. Many metallic solutions, such as those of zinc, iron, and manganese, when acidulated, yield no precipitate with it; and it is therefore often employed, in the course of analysis, to separate these metals from others which are thrown down by it in the form of insoluble sulphides. For this purpose a current of the gas is transmitted through the solution on which it is designed to act.

In these cases it is always necessary to purify it from particles held in mechanical suspension, and carried over by the effervescence of the materials employed; it is therefore first allowed to bubble up through a layer of water in a Woulfe's bottle interposed between the generator and the liquid to be submitted to its action.

When the affinity between a metallic oxide and an acid is too great to be overcome by the action of hydrosulphuric acid, the sulphide may notwithstanding be obtained, provided that an alkali be simultaneously presented to the acid of the metallic salt; this may easily be effected by mixing a soluble sulphide with the salt to be decomposed. Thus if sulphate of iron (FeO, SO_3) be exposed to a current of sulphuretted hydrogen it will experience no change; but if mixed with a solution of sulphide of potassium, a black precipitate of sulphide of iron (FeS) is immediately produced, while sulphate of potash is formed in the solution: $FeO, SO_3 + KS = KO, SO_3 + FeS$. The sulphides thus formed are very commonly hydrated compounds: when exposed to the air in their moist condition, many of them absorb oxygen rapidly, some being converted, like sulphide of nickel, into sulphate; $NiS, x\,HO + 4\,O$ yielding $NiO, SO_3, x\,HO$: whilst others are simply converted, like sulphide of iron, into free sulphur and the metallic oxide; $2\,FeS, x\,HO + 3\,O$ becoming $Fe_2O_3, x\,HO + 2\,S$.

Hydrosulphuric acid has a strong disposition to combine with the soluble sulphides. It forms definite compounds with them; thus sulphide of potassium combines with an equivalent of sulphuretted hydrogen, forming the compound (KS, HS); and sulphide of ammonium acts in a similar way, producing the ordinary test liquid (H_4NS, HS), which is used in the laboratory under the incorrect name of hydrosulphate of ammonia. These compounds emit a strong odour of sulphuretted hydrogen, and when decomposed by a metallic salt, the hydrosulphuric acid is set at liberty; for example:—

$$H_4NS, HS + MnO, SO_3 \text{ yields } H_4NO, SO_3 + MnS + HS.$$

This reaction distinguishes them from the simple sulphides. Many of the hydrosulphates and sulphides are easily detected by the odour of sulphuretted hydrogen which they evolve when moistened with hydrochloric acid. A very minute trace of the gas may be detected by placing a piece of paper moistened with acetate of lead in the upper part of the tube or vessel in which the suspected sulphide has been mixed with acid, and closing the vessel; if sulphuretted hydrogen be evolved, a brown or black tinge occurs

after the lapse of a few minutes, owing to the formation of sulphide of lead. The proportion of free sulphuretted hydrogen, or of a soluble sulphide in a solution, may be accurately determined by mixing the liquid to be tested with a small quantity of a cold solution of starch slightly acidulated with acetic acid, and adding a standard solution of iodine dissolved in iodide of potassium until the starch assumes a blue tint from the action of excess of iodine; in this reaction the sulphuretted hydrogen converts the iodine into hydriodic acid, whilst the liquid becomes milky from the separation of sulphur; $HS + I = HI + S$.

Traces of soluble sulphides may be detected in neutral or alkaline solutions by the magnificent purple liquid which they form on the addition of a solution of the nitroprusside of sodium (1353). When heated before the blowpipe, most of the sulphides emit the odour of sulphurous acid (442).

(357) PERSULPHIDE OF HYDROGEN (HS_5 ?); *Sp. Gr. of Liquid*, 1·769.—In order to procure this compound it is usual to begin by preparing a persulphide of calcium (CaS_5), which may be obtained by boiling equal weights of slaked lime and powdered sulphur in water; persulphide of calcium mixed with a corresponding amount of hyposulphite of lime is formed and enters into solution; $3\,CaO + 12\,S = CaO, S_2O_2 + 2\,CaS_5$: the undissolved sulphur is separated by filtration. On allowing the deep yellow liquid to fall into hydrochloric acid diluted with twice its bulk of water, and gently warmed, persulphide of hydrogen subsides as an oily liquid, having a smell and taste resembling that of hydrosulphuric acid: it burns with a blue flame. In many of its properties it presents a striking analogy with deutoxide of hydrogen (396); it possesses bleaching powers, is very prone to spontaneous decomposition into sulphur and sulphuretted hydrogen; it is rendered more stable by the presence of acids, and is immediately decomposed by alkalies. The latter circumstance renders it necessary in preparing this compound to add the sulphide of calcium to the acid, not the acid to the sulphide, which would be attended with an escape of hydrosulphuric acid and a precipitation of finely divided sulphur. The sulphur which is precipitated in this manner from an alkaline persulphide, was formerly employed in medicine under the term of *lac sulphuris*.

Oxides of manganese and of silver decompose persulphide of hydrogen by mere contact with the liquid, producing a violent effervescence, owing to the disengagement of sulphuretted hydrogen. Persulphide of hydrogen dissolves sulphur freely, and hence its composition is not certainly known, since a portion of sulphur

derived from the hyposulphite of lime formed in preparing the sulphide of calcium is always precipitated along with the persulphide, and becomes dissolved in the liquid obtained.

(358) BISULPHIDE OF CARBON: *Sulphocarbonic Acid* (CS_2*= 38). *Sp. Gr. of Liquid*, 1·272 at 60°; *of Vapour*, 2·6447; *Comb. Vol.* 2; *Boiling Pt.* 118·5°.—This compound may be prepared by heating fragments of charcoal to bright redness in an earthen retort, furnished with a tubulure into which is luted a porcelain tube, passing nearly to the bottom of the retort: the tube is provided at its upper extremity with a cork. From time to time this cork is withdrawn, and a fragment of sulphur is dropped into the retort; the cork is then immediately replaced, the sulphur melts, and is converted into vapour; at this elevated temperature the carbon combines with it, and the bisulphide thus obtained may be condensed in vessels properly cooled. It is yellow when first formed, and contains an excess of sulphur; but by redistillation it may be obtained in a state of purity. It is a very volatile, colourless liquid, of high refracting power, of an acrid, pungent taste, and a fœtid, peculiar, sulphurous odour. It is heavier than water, in which it is insoluble, but it is freely soluble in ether and in alcohol; when its vapour is breathed, it produces great depression followed by coma. Bisulphide of carbon has never hitherto been frozen; hence it has been employed sometimes in the construction of thermometers destined to measure very intense degrees of cold.

Bisulphide of carbon is highly inflammable, and burns with a blue flame, producing sulphurous and carbonic acid gases. It dissolves sulphur freely, and, by spontaneous evaporation, leaves it in rhombic octohedra. Phosphorus is also freely dissolved by it, and may be obtained in crystals from the solution by slow evaporation. Iodine, bromine, and chlorine are likewise readily dissolved by the bisulphide of carbon. Bisulphide of carbon offers one of the best illustrations of the analogy in properties between oxygen and sulphur; an analogy which, though far from being so complete as that of the different halogens with each other, is yet in some respects of a striking character. It is to be remarked that sulphur is the only non-metallic element excepting oxygen with which carbon can be caused to unite directly. The compound of carbon and sulphur so obtained affords a good instance of the class of combinations which Berzelius has called *sulphur-acids*, these substances possessing the power of uniting with the sulphides of

* If the formula of carbonic acid be taken as C_2O_4, that of bisulphide of carbon will be C_2S_4, and the combining volume of its vapour will be 4 instead of 2.

the basic metals, and forming with them *sulpho-salts*, corresponding in composition to analogous salts which contain oxygen :— Bisulphide of carbon, for example, may be regarded as the analogue of carbonic acid; it contains 2 atoms of sulphur in the place of 2 atoms of oxygen, the composition of the compound being the following :—

		By weight.		By vol.		Sp. gr. vap.
Carbon	C =	6 or	15·79	2 or	1·0	= 0·4146
Sulphur	S_2 =	32	84·21	2	1·0	= 2·2117
Bisulphide of carbon	CS_2 =	38	100·00	2	1·0	= 2·6263

It combines with the sulphides of the alkaline metals, forming a species of salts which are called *sulpho-carbonates*, such for instance as the sulpho-carbonate of potassium (KS, CS_2), which contains 3 atoms of sulphur in the place of the 3 atoms of oxygen in the corresponding carbonate (KO, CO_2). The soluble sulpho-carbonates are easily converted, by boiling their aqueous solutions, into carbonate of the metallic oxide; water being decomposed whilst an evolution of sulphuretted hydrogen takes place; for example :—

$$KS,CS_2 + 3\,HO = KO,\,CO_2 + 3\,HS;$$

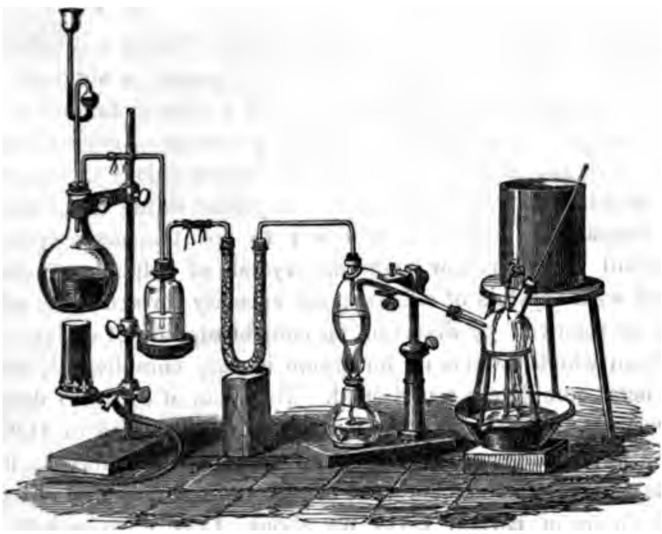
and a similar decomposition takes place slowly in the aqueous solution at ordinary temperatures. Solutions of the sulpho-carbonates of the alkaline metals give a brown precipitate with solutions of the salts of copper: they yield, with dilute solutions of nitrate of silver and of corrosive sublimate, yellow precipitates; and with salts of lead they give a red precipitate. All these precipitates blacken, more or less speedily, when kept, owing to their conversion into sulphides.

The statement of Baudrimont that a protosulphide of carbon corresponding to carbonic oxide may be formed by passing the vapour of the bisulphide over heated pumice stone, has been found by Playfair to be erroneous.

(359) Subchloride of Sulphur ($S_2Cl = 67·5$). *Sp. Gr. of Liquid*, 1·628 ; *of Vapour*, 4·70 ; *Boiling Pt.* 2·80°.—Chlorine and sulphur form two compounds with each other; they combine gradually at common temperatures, but if heated together the union is rapid. In preparing the *subchloride* of sulphur, the arrangement shown in Fig. 287 may be adopted, in which a steady current of washed and dried chlorine is directed towards the bottom of a retort containing melted sulphur; the resulting chloride must be collected in a perfectly dry receiver, kept cool: it may be purified from excess of chlorine by redistillation from powdered sulphur: a yellow volatile liquid, of penetrating, peculiar, and

disagreeable odour, is thus formed. It emits fumes on exposure to the air, owing to its action on the atmospheric moisture. When

FIG. 287.



dropped into water, it falls to the bottom, and is slowly decomposed into hydrochloric and sulphurous acids, mixed with some of the polythionic acids, and free sulphur in the electro-positive form. It acts powerfully on mercury when brought into contact with it, and dissolves sulphur freely; with ammonia it combines in two proportions, forming the compounds H_3N, S_2Cl, and 2 H_3N, S_2Cl. An oxychloride of sulphur ($S_2Cl_2O_3$)* is obtained in crystals by transmitting moist chlorine through the subchloride.

Chloride of Sulphur (SCl=51·5; *Sp. Gr. of Liquid*, 1·625) may be formed by saturating the preceding compound with chlorine; it is a deep-red liquid, which fumes strongly in the air, and is decomposed in the direct rays of the sun into subchloride of sulphur and free chlorine. It is partially decomposed by boiling it. Carius, in his elaborate examination of these compounds (Liebig's *Annal.*, cvi. 291), even denies its existence as a separate

* Two other oxychlorides of sulphur are also known, one the *chloride of thionyl* $(SOCl)_2$, corresponding to sulphurous acid in which one-half of the oxygen is displaced by chlorine. It is a colourless liquid, which boils at 179·6°, and is obtained by decomposing pentachloride of phosphorus by means of dry sulphurous acid. The other compound has already been described under the name of chlorosulphuric acid $(SO_2Cl)_2$, or *chloride of sulphuryl* (353), corresponding to sulphuric acid in which an atom of oxygen has been displaced by its equivalent of chlorine.

body, regarding the red liquid as a mixture of the subchloride with a higher chloride of sulphur (SCl_2) not yet isolated.

The *bromides* of sulphur are liquids analogous to the chlorides. The *subiodide* (S_2I) is a crystalline, brittle, steel-grey solid.

(360) BISULPHIDE OF NITROGEN (S_2N; Fordos and Gélis, *Ann. de Chimie*, III. xxxii. 389).—This compound is obtained when chloride of sulphur is dissolved in 10 or 12 times its bulk of bisulphide of carbon, and decomposed by a current of dry ammoniacal gas. The gas is transmitted till the brown colour of the precipitate which is formed disappears; the yellow liquid is filtered from the muriate of ammonia, and left to spontaneous evaporation; beautiful golden yellow rhombic crystals of sulphide of nitrogen, mixed with crystals of sulphur, are speedily formed; the sulphur may be removed by digestion in cold bisulphide of carbon. The reaction which attends its formation is very complicated, and has not been completely ascertained. Sulphide of nitrogen detonates powerfully by percussion, and explodes when heated to 314°. It has a faint odour, adheres strongly to paper if rubbed on it, and irritates the mucous membrane of the eyes and nose most painfully. Bisulphide of carbon takes up about $\frac{1}{300}$th of its weight when boiled upon it; alcohol, ether, and oil of turpentine dissolve it very sparingly; water does not dissolve it, but slowly decomposes the compound. Bisulphide of nitrogen combines with the chlorides of sulphur in several proportions.

Sulphur occurs also in a few compounds of organic origin; it enters into the composition of many fœtid volatile oils, and forms a necessary ingredient in the muscular tissue, and in several other important structures of the animal economy.

§ II. SELENIUM (Se=39·75).

Specific Gravity of Vapour at 1900°, 6·37; *of Crystals*, 4·788; *Comb. Vol.* at 1900°=1.

(361) SELENIUM is a rare elementary body, discovered during the year 1817 by Berzelius in the refuse of a sulphuric acid manufactory near Fahlun. It derives its chief interest from the remarkable analogy to sulphur which it presents. Selenium always occurs in combination; the compounds which it forms are termed *selenides*. The native selenides are very rare minerals, the most abundant of them being the selenides of iron, copper, and silver.

Preparation.—In order to obtain selenium in an isolated form, the Fahlun selenium residue is mixed with nitrate and carbonate of potash, and deflagrated; that is to say, the mixture is thrown in small quantities at a time into a red-hot crucible, in which it burns vividly. The selenium and other bodies with which it is associated are oxidized at the expense of the oxygen of the nitre. Selenic acid is formed, and by uniting with the disengaged potash of the nitre, a seleniate of potash is produced. The mass is digested in water, acidulated with hydrochloric acid, and evaporated down to a small bulk. The selenic acid is thus reduced to selenious acid (363), and the selenious acid, when treated with a current of sulphurous acid, yields a precipitate of reduced selenium as a red, flocculent, amorphous powder; $SeO_2 + 2\ SO_2$ becoming $Se + 2\ SO_3$.

Properties.—Selenium may be obtained in the amorphous, in the vitreous, and in the crystalline condition. When collected and dried, the pulverulent selenium begins to soften at a temperature below that of boiling water, and at a few degrees above 212° it melts; on cooling, it forms a brittle solid, with glassy fracture, metallic lustre, and deep brown colour, varying in specific gravity from 4·3 to 4·8. It has neither taste nor smell; it is insoluble in water, and is a non-conductor of heat and of electricity. It is soluble in oil of vitriol, forming a green solution which when diluted deposits unaltered selenium. When melted it is ductile, and may be drawn out into fine threads. The statements regarding its point of fusion are discordant, owing to its power of existing, like sulphur, in several distinct modifications. If it be maintained for some hours at 200° F.—*i.e.* below its melting point—the temperature suddenly rises till it reaches 320°, after which the selenium is found to have become granular and crystalline. The fusing point of this variety is 423° (Hittorf). It may also be obtained, with some difficulty, crystallized in minute rhomboidal prisms of sp. gr. 4·5, from its solution in bisulphide of carbon, which, at its boiling point, dissolves about 1 per cent. of vitreous selenium. If these crystals be heated to about 334° they become almost black, and increase in sp. gr. to 4·7, experiencing a molecular change, in consequence of which they are no longer soluble in bisulphide of carbon; when this black mass is melted and quickly cooled, it resumes its solubility in this menstruum owing to its reconversion into the vitreous condition. When heated in the air, selenium does not readily take fire; it burns with a blue flame, but a portion of it is volatilized in red fumes, emitting an odour resembling that of bisulphide of carbon: this is

probably due to the formation of a protoxide of selenium, which however is not acid. If heated in closed vessels, selenium boils at a temperature below a red heat, and gives off a deep yellow vapour, which, according to Deville and Troost, is of sp. gr. 8·2 at 1580°, but which when heated to 1900° F. expands, as in the case of sulphur, till it occupies a bulk equal to that of an equivalent of oxygen, when it has a sp. gr. of 6·37. The vapour condenses in red flowers or in opaque metallic-looking drops. Selenium forms two acids with oxygen; the first corresponding with sulphurous, and the second with sulphuric acid. There is also probably a lower oxide than selenious acid produced during the combustion of selenium in air, to which its peculiar odour is due, but its composition is unknown.*

(362) SELENIOUS ANHYDRIDE, or *Selenious Acid* ($SeO_2=55·7$; *Sp. Gr. of Vapour* 4·03) may be obtained by burning selenium in a current of oxygen, but it is usually prepared by boiling selenium with nitric acid or with aqua regia. The selenium is gradually oxidized and dissolved; the excess of nitric acid may be expelled by heat, leaving the selenious anhydride as a white mass, which does not melt on further urging the heat, but sublimes below redness, forming a yellow vapour, and condensing again in beautiful snow-white prismatic needles. The crystals are deliquescent; their aqueous solution is strongly acid, and has a sour burning taste. Selenious acid is speedily deoxidized by iron or by zinc, either of which, when digested in the acid, occasions the deposition of the selenium in the form of a reddish-brown powder.

Selenites.—Most of the selenites, except those of the alkalies, are insoluble in water, but soluble in nitric acid. With the alkalies three classes of salts are formed: neutral selenites, which contain 1 equivalent of acid to 1 of base, like selenite of soda (NaO, SeO_2); biselenites, with 2 equivalents of acid to 1 of base, like biselenite of soda ($NaO, HO, 2\ SeO_2+2\ Aq$); and quadriselenites, with 4 equivalents of acid to 1 of base, like quadriselenite of soda ($NaO, 3\ HO, 4\ SeO_2+Aq$). The selenites are easily recognised when heated on charcoal before the blowpipe in the reducing flame by the peculiar odour of selenium which they emit: the selenites in solution, when treated with sulphurous acid, give a reddish-brown precipitate of reduced selenium.

(363) SELENIC ACID ($HO, SeO_3=9+63·7$).—This acid is not

* The same arguments which have been urged for doubling the formulæ of sulphurous and sulphuric acids apply with equal force to the doubling of the formulæ of selenious and selenic acids, which would then be written $2\ HO, Se_2O_4$ and $2\ HO, Se_2O_6$.

known in the anhydrous form. Its solution is best obtained by deflagrating selenium or any selenite with nitre; the residue is dissolved in water, and mixed with a solution of nitrate of lead; an insoluble seleniate of lead is precipitated, and this, if suspended in water, may be decomposed by a current of sulphuretted hydrogen. Sulphide of lead is thus formed, and selenic acid is set at liberty; $PbO, SeO_3 + HS = HO, SeO_3 + PbS$. The acid may be separated by filtration, and concentrated by evaporation till it has a specific gravity of 2·6; if heated beyond 550° it is decomposed into selenious acid and oxygen. Selenic acid dissolves copper and even gold if boiled upon these metals, which are oxidized at the expense of the acid, selenious acid being disengaged; platinum is not attacked by it. Sulphurous acid is without effect upon selenic acid, but hydrochloric acid decomposes it when heated with it, chlorine and selenious acid being liberated; $HO,SeO_3 + HCl$ becoming $HO,SeO_2 + HO + Cl$. Selenic acid closely resembles sulphuric acid in its properties, and its salts are isomorphous with the sulphates of the same bases.

Seleniates.—Solutions of the seleniates give white precipitates with salts of baryta, of strontia, and of lead, owing to the formation of insoluble seleniates of these bases. These precipitates are insoluble in diluted nitric acid. When the soluble seleniates are boiled with hydrochloric acid, selenic acid is liberated, and is reduced to the form of selenious acid: sulphurous acid will then precipitate reduced selenium from the solution. Seleniate of baryta may be similarly decomposed, and may thus be distinguished from the sulphate of baryta. When heated on charcoal before the blowpipe in the reducing-flame, the seleniates emit the characteristic odour of selenium.

(364) SELENIURETTED HYDROGEN; *Hydroselenic Acid* ($HSe = 40·7$); *Sp. Gr.* 2·795.—This substance is a colourless gas, which resembles hydrosulphuric acid, but its odour is more offensive. Berzelius found that by the application of the nose to a bubble of the gas no larger than a pea, he was deprived of the sense of smell for several hours. This gas is soluble in water, and precipitates many metals from their salts in the form of selenides. Its solution, if exposed to the air, absorbs oxygen and deposits selenium. The selenides of cerium, zinc, and manganese, are flesh-coloured; most of the others are black. Seleniuretted hydrogen is obtained by acting on selenide of potassium or of iron, with diluted hydrochloric or sulphuric acid.

§ III. Tellurium ($Te=64{\cdot}5$). *Sp. Gr.* 6·65.

(364 *a*) Tellurium is a rare substance found chiefly in the mines of Hungary and Transylvania, occasionally native and nearly pure, but generally combined with various metals, such as gold, silver, bismuth, copper, or lead; it is usually also accompanied by small quantities of arsenic and selenium. Its most common ore is the black, foliated tellurium ore of Nagyag, which contains about 13 per cent. of tellurium in the form of tellurides of gold, lead, and silver, mixed with sulphides of antimony and lead. It may be extracted from this mineral by digestion of the finely-powdered ore in hydrochloric acid, which removes the sulphides of lead and antimony; the residue is washed and heated with nitric acid, the solution of nitrate of tellurium is decanted, evaporated to dryness, and treated with hydrochloric acid, after which the tellurium is thrown down as a brown powder by the addition of sulphite of soda to the acid liquid. For additional particulars regarding the extraction of tellurium, the reader is referred to the *Lehrbuch* of Berzelius (German edition, 1844, vol. ii. p. 229).

Properties.—Most English writers on chemistry class tellurium amongst the metals. It presents, however, a close analogy with sulphur and selenium, though it possesses a high metallic lustre, and resembles bismuth in colour. It fuses between 800° and 900°, and at a high temperature it is converted into a yellow vapour, and may be distilled. The distillation is best conducted by heating the tellurium very strongly in a porcelain tube, and transmitting a current of dry hydrogen gas over it; the vapour of tellurium is thus mechanically carried forward, and it is condensed in drops and flexible crystalline needles in the cooler parts of the apparatus. According to Mitscherlich, tellurium, when solidified after fusion, exhibits a rhombohedral cleavage, a circumstance which appears to indicate its isomorphism with arsenic and antimony. Tellurium is a bad conductor of heat and of electricity. When heated strongly in the air it takes fire, burns with a blue flame edged with green, and emits a peculiar characteristic odour, whilst thick white fumes of tellurous acid are produced. Like sulphur and selenium, tellurium is soluble in cold concentrated sulphuric acid, to which it gives a fine purple-red colour; on dilution it is precipitated unchanged.

Tellurium forms two oxides, (TeO_2; TeO_3) both possessed

of feebly acid characters. They correspond in composition to sulphurous and sulphuric acid.*

(364 *b*) *Tellurous Acid* ($TeO_2=80\cdot5$).—Tellurium is readily dissolved by nitric acid of sp. gr. 1·25. If the solution be poured into water immediately, a white, bulky hydrate of tellurous acid subsides. It is slightly soluble in water, reddens litmus, and combines with the alkaline bases; these compounds are soluble. Tellurous acid has a bitter metallic taste: it may be obtained in the anhydrous form, by gently heating the hydrate, or by boiling the nitric acid solution, when it is deposited in crystalline needles, which are very slightly soluble in water. The anhydride fuses easily, forming a transparent glass, which is yellow while hot, but becomes white and crystalline on cooling. Tellurous anhydride possesses considerable volatility: if fused with potash it combines with it. It also combines with the acids like many of the metallic oxides which have acid properties: these salts have a metallic taste, and are said to act powerfully as emetics. Its acid character is very feeble, and its basic property is not more strongly marked: its salts with oxalic and tartaric acid are soluble. All the soluble salts in which this oxide acts as a base are decomposed if mixed with hydrochloric acid and heated with sulphurous acid: reduced tellurium is precipitated under these circumstances. With sulphuretted hydrogen a black sulphide of tellurium is produced.

Telluric Acid ($TeO_3 = 88\cdot5$) is obtained by gently heating tellurium or tellurous acid with nitre. A tellurate of potash is formed, from which the acid is transferred to baryta, and the baryta is separated by sulphuric acid. It crystallizes in striated hexagonal prisms, which have a nauseous metallic taste; they exert but a feeble action on litmus. These crystals are composed of TeO_3, 3 HO. If heated nearly to redness they become anhydrous, and then assume an orange-yellow colour. This anhydride is completely insoluble in water, and in nitric and hydrochloric acids, as well as in alkaline solutions. Telluric acid has but a feeble affinity for bases, but it forms salts which contain 1, 2, and 4 atoms of the acid to each atom of base. Laurent suggests that these different classes of salts probably contain different modifications of the acid analogous to stannic and metastannic acids (678). Their solutions, when acidulated, yield a black precipitate with sulphuretted hydrogen. When telluric acid, or one of its salts, is heated to redness,

* Those who double the formulæ of sulphurous and sulphuric acid, extend the same rule to the compounds of tellurium with oxygen, tellurous acid becoming Te_2O_4, and telluric acid Te_2O_6.

oxygen is disengaged and the telluric is converted into tellurous acid.

Two *chlorides*, TeCl and $TeCl_2$, have been obtained by the direct action of chlorine upon tellurium; both of them are volatile, the vapour of the protochloride is of a violet colour; they are decomposed by a large quantity of water.

(364 *c*) TELLURETTED HYDROGEN ($TeH=65.5$); *Sp. Gr.* 4·489; *Comb. Vol.* 2.—The most interesting compound of tellurium is that which it forms with hydrogen. It is a gaseous body analogous to sulphuretted hydrogen, and is possessed of feebly acid properties. It may be obtained by decomposing the alloy of tellurium with zinc or tin, by means of hydrochloric acid. The gas which escapes burns with a blue flame; it reddens litmus, and has an odour which cannot be distinguished from that of sulphuretted hydrogen: with water it forms a colourless solution, which becomes brown by exposure to the air, owing to the oxidation of the hydrogen and separation of tellurium. Telluretted hydrogen precipitates most of the metals from their solutions, in the form of tellurides which have a close analogy with the corresponding sulphides. The tellurides of the alkaline metals are soluble in water.

Tellurium, whether in the form of a soluble tellurite or in that of a tellurate, is thrown down from its solutions in the reduced form by zinc or iron; neutral solutions of the salts of both its acids are also reduced by protosulphate of iron and by protochloride of tin; in these cases the tellurium falls in brown flocculi. The tellurates of the alkalies when heated to redness in a tube with charcoal are reduced to tellurides, which are soluble in water, and form a red liquid.

§ IV. PHOSPHORUS ($P=31$).

Comb. Vol. of Vapour, 1; *Calcd. Sp. Gr. of Vapour*, 4·284; *Observed Sp. Gr. of Vapour*, 4·42.

(365) PHOSPHORUS was discovered by Brandt in 1669. It is never met with in nature in the uncombined state, but it occurs in small proportion as phosphate of lime, as a constituent of the primitive and volcanic rocks, by the gradual decay of which it passes into the soil: from the soil it is extracted by plants, which accumulate it, particularly in their seeds, in quantity sufficient for the support of the various tribes of animals which they supply with food. In the animal system it is collected in large amount, and when combined with oxygen and lime, as phosphate of lime,

forms the principal earthy constituent of the bones of the verte-ata. Phosphorus also appears to be essential to the exercise of e higher functions of the animal, since it exists as a never-fail-g ingredient in the substance of which the brain and nerves are mposed. It is likewise contained in albumen and in fibrin in iall proportions, and is present in the form of phosphates of the rths and of the alkalies in the urine and solid excrements of iimals.

Preparation.—Phosphorus was originally extracted from the lts contained in urine, but it is now obtained almost exclusively om the bones of animals. In order to prepare it, bones are irned to whiteness by calcining them in an open fire for some urs; they are then reduced to powder; 3 parts of this bone-h are mixed with 2 of concentrated sulphuric acid, and 18 or 20 rts of water. The mixture is allowed to stand for two or three ys, after which it is placed upon a strong linen filter, and the id liquid is separated from the sulphate of lime by pressure; the sidue is further washed with water, and the washings are added the filtered solution. In this process the sulphuric acid is lded in such quantity as partially to decompose the phosphate of me; two-thirds of the lime are removed by it in the insoluble rm, as sulphate of lime, the remaining third being left in combi-ation with the whole of the phosphoric acid, with which it forms compound readily soluble in water, frequently described as *super-hosphate of lime* ($2\,HO,CaO,PO_5$). The reaction may be thus pressed in symbols :—

$$\overbrace{3\,CaO,PO_5}^{\text{Bone ash.}} + \overbrace{2\,(HO,SO_3)}^{\text{Sulph. acid.}} = \overbrace{2\,HO,CaO,PO_5}^{\text{Superphosph. lime.}} + \overbrace{2\,(CaO,SO_3)}^{\text{Sulph. lime.}}$$

This acid solution is evaporated to the consistence of a syrup, hen mixed with one-fourth of its weight of charcoal, and heated o incipient redness in an iron pot, stirring constantly. The mass, hen dry, is transferred to an earthen retort (*a*, fig. 288), which is overed externally with a thin paste, consisting of a mixture of qual parts of borax and fire-clay, with the view of rendering the etort less porous. It is then exposed to a heat which is slowly ised to a full red. Phosphorus gradually rises in vapour, and is onveyed by means of a wide copper tube, bent as at *b*, so as to ip into water contained in a vessel provided with a smaller tube, pen at both ends, for conveying the uncondensed gases into a himney. The phosphorus is condensed in yellow drops. In this peration it is found necessary to convert the phosphate into uperphosphate of lime, since the bone-ash, when heated with

charcoal, does not part with its phosphorus. The superphosphate of lime in contact with charcoal is decomposed; the lime retains sufficient phosphoric acid to reconstitute bone-earth, which remains unchanged in the retort, while the excess of acid and the water which the mass always retains are decomposed by the charcoal; hydrogen, carbonic oxide, and phosphorus are the results. Gaseous matters escape, therefore, during the whole operation, which may be regarded as consisting of two stages, the first being the decomposition of the superphosphate of lime into bone-ash and hydrated phosphoric acid:—

FIG. 288.

$$3\ (2\ HO,CaO,PO_5) = 3\ CaO,PO_5 + 2\ (3\ HO,PO_5),$$

whilst the second stage consists of the deoxidation of the liberated acid:—

$$2\ (3HO,PO_5) + 16\ C = 2\ P + 6\ H + 16\ CO.*$$

With a view to render the phosphorus perfectly pure, it is fused under warm water, squeezed through wash-leather, and again melted, first under ammonia, and then under a solution of bichromate of potash in diluted sulphuric acid. The easy fusibility of phosphorus enables it to be moulded into sticks with facility; it is melted under water and forced into tubes, in which it is allowed to solidify.

Properties.—Phosphorus is a soft, semi-transparent, colourless, waxy-looking solid, which fumes in the air, emitting white vapours of an alliaceous odour. It has a specific gravity of 1·83 at 50° (Schrötter). It fuses at 111·5°, and if melted under an alkaline liquid and allowed to cool undisturbed, it will long continue fluid at ordinary temperatures, but when touched with a wire or a glass rod it solidifies suddenly. It is extremely inflammable, taking fire in the open air at a temperature very little above its fusing

* If sand be mixed with the superphosphate of lime in the above process, the whole of the phosphoric acid is economized, since the silicic acid combines with the lime and liberates the portion of phosphoric acid which would otherwise be retained.

point. If it contain impurities, such as oxide of phosphorus, it takes fire still more easily. Great caution is therefore required in handling it; it is better always to cut it under water. The burns occasioned by melted phosphorus are deep and often extremely severe, from the difficulty of extinguishing the flame.

Phosphorus burns with a brilliant white flame, and emits dense white fumes of phosphoric acid. In closed vessels it boils at about 550°, giving off a colourless vapour, of which 100 cubic inches weigh about 135 grains. An equivalent of phosphorus, therefore, gives off a volume of vapour equal to that of an equivalent of oxygen; and according to Deville, no alteration in the relative volumes of the two is effected by a temperature of 1900°. Phosphorus is insoluble in water; it is slightly soluble in ether, but more so in benzol, in oil of turpentine, and in the fixed and essential oils. It is also freely dissolved by subchloride of sulphur, and by the bisulphide of carbon; by allowing its solution in one of these liquids to fall upon filtering paper in the open air, the finely divided phosphorus absorbs oxygen so rapidly that it takes fire as soon as the solvent has evaporated. If the solution be allowed to evaporate slowly in a current of hydrogen or carbonic acid, the phosphorus may be obtained crystallized in rhombic dodecahedra.

Phosphorus is always preserved under water, for when exposed to the air, at all temperatures above 32° it gradually combines with oxygen, and undergoes a slow combustion; under these circumstances in a darkened room it emits a pale greenish light (hence its name, from φῶς 'light,' φορὸς 'bearing'), attended with the production of the white fumes and the garlic odour already mentioned. The luminosity of phosphorus is prevented by the admixture of certain inflammable vapours and gases in minute quantity with the atmosphere; if air be mixed with either $\frac{1}{450}$th of its bulk of olefiant gas, $\frac{1}{1820}$th of naphtha, or $\frac{1}{4444}$th of oil of turpentine, a stick of phosphorus no longer appears luminous when exposed to its action (Graham).

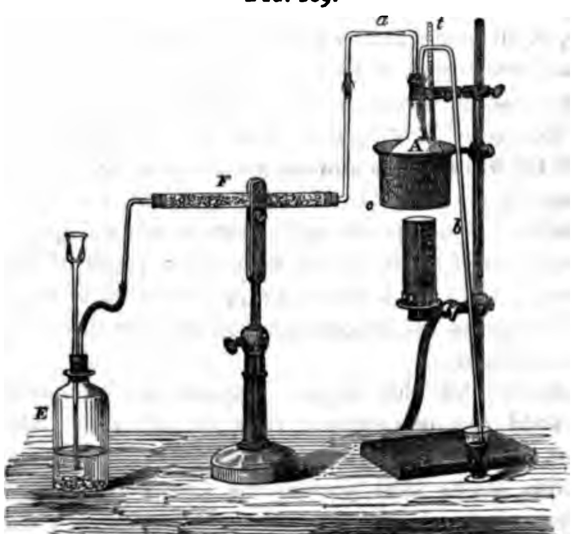
It is remarkable that in pure oxygen the luminosity is not observed until the temperature rises to 60°, unless the gas be rarefied, or be diluted with some other gas.

Berzelius states that phosphorus may become luminous at ordinary temperatures without undergoing oxidation, but simply from its volatilization, and that the emission of light occurs in hydrogen, nitrogen, and even in the vacuum of the barometer; but Schrötter has shown, by careful and conclusive experiments, that in all cases where light appears to be emitted during this volatilization, it is due to the presence of traces of oxygen (*Chem. Gaz.*, xi. 312).

(366) *Different forms of Phosphorus.*—Phosphorus assumes several different forms under the influence of causes apparently trifling. The *transparent* variety has been already mentioned; this, when kept exposed to light under water, assumes a second form, which is *white* and opaque, and somewhat less fusible. It has a sp. gr. of 1·515: white phosphorus becomes reconverted into the vitreous variety by a temperature not exceeding 122°. A third form is obtained by suddenly cooling melted phosphorus; it is perfectly *black* and opaque; whilst a fourth or *viscous* modification, analogous to viscous sulphur, may be obtained by heating very pure phosphorus to near its boiling point and suddenly cooling it. A fifth form occurs in the shape of *red* scales, which are obtained by the spontaneous sublimation of phosphorus in the Torricellian vacuum when exposed to the rays of the sun.

Red or *amorphous Phosphorus.*—The red form of phosphorus has been carefully studied by Schrötter (*Ann. de Chimie,* III. xxiv. 406). It may be obtained by placing a quantity of dried common phosphorus in the bulb of a flask, A, fig. 289, to the neck of which a long narrow tube, *b*, bent

FIG. 289.



downward, is attached; the open end of this tube dips into a little mercury; the air in the flask is displaced by means of a current of carbonic acid, which is supplied from the bottle E, and dried by passing through the tube, F, filled with

chloride of calcium; the tube is then sealed at the narrow portion, *a*, and the apparatus which supplied the carbonic acid is removed. Heat is next applied to the flask by means of an oil bath, *c*: the phosphorus melts readily, but by regulating the heat steadily between 450° and 460°, by means of the thermometer, *t*, and maintaining it for 30 or 40 hours, almost all the phosphorus will become converted into the solid amorphous variety. When the change appears to be complete, the apparatus is allowed to cool: bisulphide of carbon is then poured upon the mass in the flask, and digested on it for some hours; this is poured off, and fresh bisulphide added, the digestion being repeated as long as any phosphorus is dissolved; this may be known by allowing a few drops of the decanted liquid to evaporate spontaneously in a watch-glass; any dissolved phosphorus will be left behind.

The red powder of which the undissolved portion consists, if not quite free from unaltered phosphorus, takes fire spontaneously when exposed to the air; if quite pure, it does not take fire; but it absorbs oxygen very slowly, the oxidation being more rapid if the powder be moist; phosphorous acid is gradually formed, and from its deliquescent character the powder becomes damp. This oxidation occurs so slowly that it was at first imagined that amorphous phosphorus underwent no change by exposure to the air. The higher the temperature at which the transformation is effected, the deeper is the colour of the product, which in the finest specimens rivals that of vermilion. By heating the phosphorus more strongly during its preparation, the change may be produced much more rapidly, but the phosphorus then assumes the form of coherent flakes, which are more difficult to purify and to detach from the vessel in which they are prepared. This form of phosphorus has been manufactured at Birmingham on a considerable scale. The process, however, is not unattended with danger; for if the red powder be heated up to the point at which its re-conversion into the transparent variety takes place, the whole mass suddenly passes back into the ordinary form, with a copious evolution of heat, followed by the sudden formation of a large volume of the vapour of phosphorus. The changes produced in phosphorus by heat may be readily watched by placing a few fragments of well-dried phosphorus in a tube, upon which two or three bulbs have been blown, then expelling the air by a current of carbonic acid, and sealing one end of the tube,—the open end being made to dip into mercury. On applying heat to the phosphorus it becomes red, but on continuing to raise the temperature it distils over in perfectly colourless transparent drops, which frequently

remain liquid for some hours, though they ultimately solidify to a transparent colourless mass.

Red or amorphous phosphorus differs remarkably in many of its properties from the waxy-looking stick phosphorus. It may be exposed to the air without emitting any odour. It is not soluble in either bisulphide of carbon, terchloride of phosphorus, or benzol. The density of amorphous phosphorus exceeds that of the vitreous form; the red powder, according to Brodie, having a specific gravity of 2·14. It may be heated in the open air without change till the temperature reaches 500°; at this point it melts and bursts into flame, and burns with the dazzling brilliancy of common phosphorus, emitting dense fumes of phosphoric acid. Chlorine acts directly upon red phosphorus without the application of heat: the temperature rises, but the phosphorus does not take fire. When rubbed with chlorate of potash it detonates, very slight friction being sufficient to produce the action: peroxide of manganese and peroxide of lead act with it in a similar way, but less readily. Schrötter has attempted, though as yet with imperfect success, to apply this form of phosphorus to the preparation of lucifer matches. Immense quantities of phosphorus are consumed in this manufacture. In the usual mode of preparing these matches, the ends of the pieces of wood are first gummed and dusted over with sulphur, and then tipped with a mixture, in which the chief ingredients are an emulsion of phosphorus in glue, and chlorate of potash, or oxide of manganese. The manufacture is one attended with danger, from the highly inflammable and explosive nature of the ingredients used; but, in addition to this risk, those employed in the business are liable to a distressing form of caries of the lower jaw, arising from the action of the fumes of phosphorus upon those who inhale them. Of these evils, the first would be greatly lessened, and the second altogether avoided, by the use of amorphous phosphorus.

Although vitreous phosphorus acts as a powerful irritant poison upon animals when taken internally, the amorphous variety may be swallowed with impunity; the vitreous phosphorus forms the active ingredient in the phosphorus paste frequently used to destroy cockroaches and other kinds of vermin.

Owing to its strong affinity for oxygen, phosphorus reduces some of the oxidized compounds of the metals to the metallic state: a stick of phosphorus placed in a solution of chloride of gold or of nitrate of silver, becomes speedily incased in reduced gold or silver. Salts of palladium, platinum, and copper, are also reduced

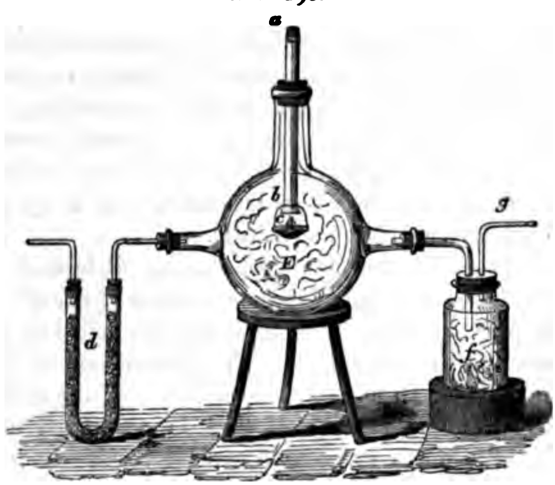
gradually when a stick of phosphorus is immersed in their solutions.

(367) OXIDES OF PHOSPHORUS.—Phosphorus forms four well defined compounds with oxygen: three of them possess an acid character. The following table shows the composition of these different oxides:—

		In 100 parts.	
		Phosphorus.	Oxygen.
Phosphoric anhydride	$PO_5 = 71$	43·66	56·34
Phosphorous ditto	$PO_3 = 55$	56·36	43·64
Hypophosphorous ditto (hypothetical)	$PO = 39$	79·44	20·56
Oxide of phosphorus	$P_2O = 70$	88·57	11·43

(368) PHOSPHORIC ACID ($PO_5=71$): *Phosphoric Anhydride.*—The most important of the oxides of phosphorus is phosphoric acid, which occurs native in considerable quantity in the form of phosphate of lime. The anhydride of this acid is the sole product of the rapid combustion of phosphorus in dry oxygen or in atmospheric air. By means of the apparatus shown in fig. 290, a large quantity of phos phoric anhydride may be readily obtained in a few hours: E is a three-necked globe, in the centre of which is suspended a porcelain dish, *c*; this dish is attached by means of platinum wire

FIG. 290.



to the wide tube, *a b*, which is closed at *a* with a cork; the bottle, *f*, is connected by the tube, *g*, with an aspirator, or other convenient means of maintaining a continuous current of air through the apparatus: the air as it enters is thoroughly dried by passing over pumice moistened with sulphuric acid, in the tube, *d*. A fragment of well dried phosphorus is placed in the dish, *c*, and kindled by touching it with a hot wire. As the phosphorus burns away fresh pieces are added through

the aperture *a*, which is again immediately closed with the cork. The anhydride thus obtained generally contains traces of one of the lower oxides of phosphorus. It forms a snow-white, flocculent, non-crystalline, anhydrous, but extremely deliquescent, powder. When dropped into water it combines with it, emitting a hissing noise; the greater part is instantly dissolved, leaving a few gelatinous flocculi, which slowly disappear. After it has once been dissolved, it cannot again be completely deprived of water, unless it be made to enter into combination with a base, such as soda or oxide of lead: the base in this case unites with the acid and displaces the water. It does not emit vapour at ordinary temperatures, and owing to its powerful affinity for water, this anhydride is often used as a desiccating and dehydrating agent; and for this purpose it surpasses in efficacy almost every known substance.

(369) *Hydrates of Phosphoric Acid.*—In a hydrated state the acid is generally procured by boiling 1 part of phosphorus in 13 parts of nitric acid of sp. gr. 1·20. The phosphorus becomes oxidized by the nitric acid, which is decomposed with escape of deutoxide of nitrogen, and the phosphoric acid is dissolved as it is formed. When the phosphorus has all disappeared, the excess of nitric acid is expelled by evaporating the liquid in a platinum vessel until dense white fumes begin to arise: on cooling, the acid solidifies to a transparent glassy mass, frequently termed *glacial phosphoric acid*. This glacial acid is extremely deliquescent, producing a solution which, when saturated, has a sp. gr. of 2·0. It is intensely acid, but not caustic.

The oxidation of phosphorus by nitric acid furnishes an easy means of ascertaining the composition of phosphoric acid. For this purpose, 31 grains of phosphorus are boiled in a glass retort with pure diluted nitric acid. The greater part of the excess of water and nitric acid having been distilled off, the acid solution is added to 350 grains of oxide of lead, in a weighed platinum dish: the liquid is slowly evaporated and the residue ignited; by a red heat the whole of the nitric acid is expelled, and the phosphoric acid alone remains in combination with the oxide of lead. The oxide and acid together will be found to weigh 421 grains, showing an increase in weight upon the phosphorus and oxide of lead of 40 grains: 31 parts of phosphorus therefore require 40 parts of oxygen for conversion into phosphoric acid.

A less pure acid is procured by adding to a solution of superphosphate of lime (prepared from bones by the process already described as a preliminary step towards procuring phosphorus)

carbonate of ammonia till effervescence ceases; tribasic phosphate of lime is precipitated, leaving phosphate of ammonia in solution. The precipitated phosphate of lime is separated by filtration, the liquid evaporated to dryness, and the residue ignited. Ammonia is expelled, and phosphoric acid (contaminated with all the soluble salts which the bones contained) remains behind.

Hydrated phosphoric acid cannot be completely deprived of water by ignition; for when heated to redness, the acid sublimes with the water. There are three different hydrates of phosphoric acid, each of which possesses the properties of a distinct acid: viz.—

The protohydrate of phosphoric acid . . . HO,PO_5,
The deutohydrate of phosphoric acid . . $2\ HO,PO_5$,
The tritohydrate of phosphoric acid . . . $3\ HO,PO_5$.

These different hydrates of the acid retain their peculiar characteristics when dissolved in water, and combine with 1, with 2, or with 3 equivalents of bases to form salts, according as the protohydrate, the deutohydrate, or the tritohydrate is employed. Owing to the important influence which the study of these compounds has exercised upon the theory of saline combinations in general, it will be necessary to examine them somewhat in detail.

(370) *Tritohydrate* or *Tribasic Phosphoric Acid* ($3\ HO,PO_5$). If the liquid formed by dissolving the glacial acid in water be boiled for some time, and carbonate of soda be then added until the solution becomes slightly alkaline, a tribasic phosphate of soda and water is obtained, which on evaporation crystallizes in large transparent rhombic prisms ($2\ NaO,HO,PO_5+24\ Aq$). If this solution be mixed with a neutral solution of nitrate of silver, a canary-yellow precipitate of tribasic phosphate of silver ($3\ AgO,PO_5$) is formed. Although this solution was neutral or slightly alkaline before admixture with nitrate of silver, it will be found afterwards to have a decidedly acid reaction upon litmus, nitric acid having been liberated:—

$$2\ NaO,HO,PO_5+3\ (AgO,NO_5)=2\ (NaO,NO_5)+HO,NO_5+3\ AgO,PO_5.$$

Acetate of lead may be used as a precipitant instead of nitrate of silver, and in this case a white tribasic phosphate of lead ($3\ PbO,PO_5$) subsides. If this phosphate of lead be well washed, suspended in water, and exposed to the action of a current of sulphuretted hydrogen, pure tritohydrate of phosphoric acid is liberated and becomes dissolved in the liquid, whilst the black insoluble sulphide of lead is formed; $3\ PbO,PO_5+3\ HS=3\ HO,PO_5+3\ PbS$. The sulphide of lead may be removed by filtration, and the acid obtained

in deliquescent crystalline plates, by evaporation *in vacuo* over sulphuric acid. It requires 3 atoms of a base for saturation. The salts of this hydrate form the common *tribasic phosphates*.

There are three varieties of these phosphates; viz., 1, those with 3 atoms of a metallic protoxide, such as the tribasic phosphate of soda ($3\,NaO,PO_5+24\,Aq$); these salts when soluble have a strongly alkaline reaction: 2, those with 2 atoms of a basic protoxide of a metal and 1 atom of basic water (291) like the ordinary phosphate of soda ($2\,NaO,HO,PO_5+24\,Aq$); the soluble salts of this class are neutral, or have a very feebly alkaline reaction: and 3, those with only 1 atom of fixed base with 2 atoms of basic water, of the form of the salt ($2\,NaO$, HO, $PO_5+2\,Aq$) frequently called the biphosphate of soda; these salts have a strongly acid reaction, and are often spoken of as the *superphosphates*.

The soluble salts of this variety of phosphoric acid are characterized by the yellow phosphate of silver which their neutral solutions form with nitrate of silver; this precipitate is freely soluble both in nitric acid and in ammonia. They also yield a crystalline precipitate when a clear solution of sulphate magnesia, rendered alkaline by ammonia, is briskly stirred with them; this precipitate is insoluble in water which contains free ammonia; it consists of ($2\,MgO,H_4NO,PO_5+12\,Aq$): when ignited, the water and ammonia are expelled, and it becomes converted into pyrophosphate of magnesia ($2\,MgO$, PO_5), a compound frequently employed as a means of estimating the amount of phosphates in solutions which contain them; 100 parts of the ignited residue containing 64·0 of PO_5. Neutral solutions of the phosphates give precipitates with salts of baryta and of lime; the phosphates of baryta and lime are readily soluble in acetic acid. The quantity of phosphoric acid in a solution may also be ascertained, if neither sulphuric nor hydrochloric be present, by means of acetate of lead; the solution, before this salt is added to it, should be neutralized by ammonia, and then acidulated freely with acetic acid; the precipitate ($2\,PbO$, HO,PO_5) should be well washed and ignited, by which means it is rendered anhydrous. 100 parts of the ignited residue represent 23·65 of anhydrous phosphoric acid. Chancel has lately shown that the acid solution of nitrate of bismuth furnishes an admirable method of separating phosphoric acid from many bases, such as iron, lime, and alumina, which form phosphates soluble only in acidulated liquids. Care is requisite to remove any chlorine or sulphuric acid from the liquid before adding the solution of bismuth, which is prepared by dissolving 1 part of the crystallized nitrate in 4

parts of nitric acid of sp. gr. 1·36, adding 30 parts of water, then boiling, and filtering if necessary. In separating the phosphate of bismuth by this reagent, the liquid must be boiled, and the precipitate well washed with boiling water and carefully dried: 100 parts of the phosphate of bismuth (BiO_3,PO_5) contain 23·28 of phosphoric acid (PO_5). With sesquioxide of iron phosphoric acid forms an insoluble buff-coloured precipitate ($Fe_2O_3,PO_5 + 4\ Aq$), which is also sometimes employed to estimate the quantity of phosphoric acid in a solution.

(371) *Deutohydrate*, or *Pyrophosphoric Acid* ($2\ HO,PO_5$).—When rhombic phosphate of soda ($2\ NaO,HO,PO_5 + 24\ Aq$) is exposed to heat, it melts in its water of crystallization; and by continuing to apply to it a temperature not exceeding 300°, it may be reduced to a hard, white, saline mass, which may be redissolved in water with all its former properties. The dry mass consists of $2\ NaO,HO,PO_5$. If, however, it be heated to redness before redissolving, 1 atom of water is expelled: the residue is found to consist of $2NaO,PO_5$, and the phosphoric acid is reduced to the dibasic variety: for on redissolving it in water and evaporating the solution, the liquid no longer yields rhombic crystals, but furnishes acicular crystals, composed of $2\ NaO,PO_5 + 10\ Aq$; and the solution, instead of yielding a yellow precipitate with nitrate of silver, now gives a white one, consisting of $2\ AgO,PO_5$. In this case the solution, if neutral to litmus before intermixture with the silver salt, remains neutral afterwards, because no free acid is liberated:—

$$2\ (AgO,NO_5) + 2\ NaO,PO_5 = 2(NaO,NO_5) + 2\ AgO,PO_5.$$

With a solution of acetate of lead the dibasic phosphate of soda also occasions a white precipitate, the composition of which is represented by the formula $2\ PbO,\ PO_5$: and if the lead salt be decomposed with sulphuretted hydrogen, it yields the deutohydrate of phosphoric acid ($2\ HO,PO_5$). The excess of sulphuretted hydrogen must be got rid of by exposure to the air (not by heat, otherwise the tribasic hydrate of the acid is formed), and the acid may be obtained in crystals by evaporation *in vacuo* over sulphuric acid. The dibasic phosphate of soda, from the mode in which it is obtained, is often termed the *pyrophosphate* of soda, and the corresponding dibasic salts of the acid, *pyrophosphates*. No solid pyrophosphate of potash or of ammonia can be obtained; these salts are stable while in solution, but on evaporation they become converted into tribasic phosphates by the assimilation of water (Graham). Two classes of pyrophosphates may be procured;

one with two atoms of fixed base, like the ordinary pyrophosphate of soda ($2\ NaO,PO_5 + 10\ Aq$), the other corresponding in composition to the acid pyrophosphate of soda (NaO,HO,PO_5) in which an atom of water has taken the place of one of the atoms of fixed base in the ordinary salt.

(372) *Protohydrate*, or *Metaphosphoric Acid* (HO, PO_5).—If, in preparing the rhombic phosphate of soda (370), two equal portions of phosphoric acid be taken, and after neutralizing one portion with carbonate of soda, as above directed, the second quantity of acid be added to the neutralized solution, a tribasic phosphate of soda, consisting of $NaO, 2\ HO,PO_5$, will be obtained on evaporating the liquid to dryness; but on igniting the residue, the 2 atoms of water will be expelled, and a fusible monobasic phosphate, or *metaphosphate*, of soda (NaO,PO_5) will remain in the form of a transparent glass. This, if dissolved in water, gives with nitrate of silver a gelatinous white precipitate, different in appearance and composition from either of the former phosphates of silver; it contains AgO,PO_5, and is soluble in excess of the soda salt. With acetate of lead a white precipitate also is formed (PbO,PO_5); it is fusible in boiling water, and when decomposed with sulphuretted hydrogen it yields the protohydrate of the acid (HO,PO_5), which is distinguished from the other hydrates by its power of coagulating the albumen of white of egg. Acetic acid does not coagulate albumen, neither does a solution of metaphosphate of soda; but if the two solutions be mixed, the acetic acid liberates metaphosphoric acid, and the albumen becomes coagulated. Metaphosphate of soda is capable of combining with water of crystallization, and retains 1 atom if dried at 212°; this water is not basic, for on again dissolving the salt, it gives the usual reactions of the metaphosphates. If, however, the salt be heated to 300°, it does not lose weight, but becomes converted into the acid pyrophosphate of soda, the water by the application of heat having changed its function in the salt, and having now become basic (Graham):—

$$\overbrace{NaO,PO_5 + HO}^{\text{Hydrated metaphosphate.}} \text{ becomes } \overbrace{NaO,HO,PO_5}^{\text{Pyrophosphate of soda and water.}}.$$

This change of properties in the salt, without any change in the proportions of its components, here admits of a satisfactory explanation; and it is a striking and instructive illustration of the facility with which chemical compounds, by a change in molecular constitution, may sometimes give rise to substances, the properties of which may be very different, though the results of their analysis in 100 parts may numerically coincide.

Metaphosphate of soda forms with salts of baryta a white insoluble metaphosphate of baryta (BaO, PO_5); but this precipitate when boiled becomes gradually dissolved, assimilating 2 atoms of water, and becoming converted into the acid tribasic phosphate of baryta ($BaO, 2\ HO, PO_5$). The compounds of this hydrate of phosphoric acid are all monobasic. Their solutions redden litmus feebly.

The aqueous solution of the protohydrate of phosphoric acid, when boiled, becomes converted into the tritohydrate, consequently it cannot be concentrated by the action of heat: but the solution may be preserved at common temperatures without change.

Most of the preceding facts relating to the phosphates are drawn from the important investigations of Graham (*Phil. Trans.*, 1833).

Modifications of Metaphosphoric Acid.—Fleitmann and Henneberg (*Liebig's Ann.*, lxv. 324) have described two new classes of phosphates intermediate between the metaphosphates and pyrophosphates. By melting pyrophosphate and metaphosphate of soda together, in the proportion of an atom of each, they obtained a salt consisting of $3\ NaO, 2\ PO_5$; and by fusing 4 atoms of the metaphosphate of soda with 1 atom of the pyrophosphate, a definite soda salt was obtained, which consisted of $6\ NaO, 5\ PO_5$; both these salts are very unstable, and in solution pass quickly into a mixture of pyrophosphate and metaphosphate. Definite salts of silver and of magnesia corresponding to these compounds were obtained.

If the glassy metaphosphate of soda be fused, and allowed to cool very slowly, it furnishes a very beautiful crystalline mass, which, when dissolved in a small quantity of hot water, forms a liquid which divides into two strata; the smaller of these contains unchanged metaphosphate of soda; but the bulk of the liquid is a solution of the crystalline salt, which may be obtained on evaporation: this solution is *neutral* and has a saline taste, whilst that of the ordinary or vitreous metaphosphate is insipid. The crystalline salt, by boiling, is rapidly converted into the *acid* common phosphate ($NaO, 2\ HO, PO_5$); a silver salt, consisting of $3\ (AgO, PO_5) + 2\ HO$, may be obtained from the crystalline soda salt by precipitation.

Maddrell (*Proceed. Chem. Soc.*, 1847, p. 273) has described a series of monobasic metaphosphates which are anhydrous, crystalline, and insoluble in water, but soluble in oil of vitriol. They were formed by heating a solution of the sulphate or nitrate of the base with an excess of phosphoric acid, until the sulphuric or other acid of the salt was expelled. Salts of potash, soda, alumina,

copper, nickel, &c., were thus procured. The soda salt, if prepared with phosphoric acid which contains magnesia, or any base isomorphous with it, forms an insoluble double metaphosphate: the magnesian double salt is crystalline, and consists of [3 (MgO, PO_5). NaO, PO_5].

(373) PHOSPHOROUS ANHYDRIDE (PO_3) may be procured by burning phosphorus in a limited current of dry air. A white, volatile, deliquescent, inflammable powder, destitute of crystalline structure, is thus obtained, often mixed with small quantities of oxide of phosphorus, and phosphoric anhydride.

The *hydrated acid* may be obtained in solution by transmitting a stream of chlorine very slowly through a deep layer of phosphorus melted under water, so that each bubble of gas shall be completely absorbed by the phosphorus; terchloride of phosphorus (PCl_3) is formed, and is immediately decomposed by the water into hydrochloric and phosphorous acids; $PCl_3 + 6\,HO = 3\,HO,PO_3 + 3\,HCl$. If the acid liquid be concentrated by a heat not exceeding 400°, hydrochloric acid is expelled, and hydrated phosphorous acid is obtained in deliquescent rectangular prisms, ($2\,HO,PHO_4$). When exposed to the air it gradually absorbs oxygen,; and by a high temperature it is decomposed into phosphoric acid and phosphuretted hydrogen (376). It is also furnished in a less pure form, by the slow combustion which occurs when phosphorus is left exposed to the action of the atmosphere; this may be safely effected by placing sticks of phosphorus separately in tubes open at both ends, the lower aperture of the tube being a little contracted to prevent the phosphorus from falling out; a number of these tubes are then placed in a funnel, and the dense acid liquid which is gradually formed drains into a vessel placed for its reception. In this process phosphorous acid is first produced; the acid being deliquescent attracts moisture from the air, and then, by gradually absorbing oxygen, it forms phosphoric acid. The oxidation never proceeds so far as to convert the whole into phosphoric acid; the liquid therefore contains a mixture of phosphorous and phosphoric acids, which was at one time supposed to be a peculiar oxide of phosphorus, and was termed *phosphatic acid.*

Phosphites.—Phosphorous acid is dibasic; that is, its normal salts contain 2 atoms of base; but Wurtz finds that hydrated phosphorous acid, besides its two basic atoms of water, retains a third atom of water, which is essential to it. Neutral phosphite of soda, for instance, consists of ($2\,NaO,PHO_4 + 10\,Aq$); when heated to 572°, it still retains 1 atom of water, and consists of $2NaO,PHO_4$. Acid phosphites may also be formed: the acid

phosphite of baryta, dried at 212°, consists of (BaO,HO,PHO_4). The acid phosphites when heated emit hydrogen gas, whilst a monobasic phosphate remains behind; thus (BaO,HO,PHO_4) becomes $BaO,PO_5+2\,H$. If the phosphite contain a smaller quantity of water, phosphuretted hydrogen is also emitted; for instance, in the case of phosphite of lead, $5(2\,PbO,PHO_4)$ yield $10\,PbO,\ 4\,PO_5+H_3P+2\,H$. Free phosphorous acid does not immediately reduce permanganate of potash, unless heated with it; a reaction which distinguishes it from hypophosphorous acid, which, even in the cold, rapidly discharges the colour of the permanganate in acid solutions. The phosphite of lead is the least soluble of the phosphites; it is insoluble in acetic acid. With a solution of corrosive sublimate (HgCl), acidulated with acetic acid, the phosphites give a white precipitate of calomel, the formation of which is hastened by heating the liquid. Another characteristic reaction is the reduction of sulphurous acid by a solution of the phosphites, with evolution of sulphuretted hydrogen:—

$$3\,(2\,HO,PHO_4)+2\,SO_2+2\,HO = 3\,(3\,HO,PO_5)+2\,HS.$$

(374) HYPOPHOSPHOROUS ACID, (HO,PH_2O_3; Wurtz).—This compound was formerly considered to be an acid of phosphorus with a still smaller quantity of oxygen than the preceding, but it has never been obtained in the anhydrous form. It is produced whenever phosphorus is boiled with a solution of caustic potash or soda, or with a hydrate of one of the alkaline earths. In a hydrated condition it may be procured by Rose's method of boiling phosphorus with baryta in water; phosphuretted hydrogen escapes, and on evaporation a baryta salt is obtained, composed of BaO, PH_2O_3, owing to the following decomposition; $3\,(BaO,HO)+4\,P+6\,HO=3\,(BaO,PH_2O_3)+H_3P$; and on adding sulphuric acid cautiously, pure hypophosphorous acid is obtained in solution, whilst the baryta is separated as sulphate of baryta. The hypophosphite of baryta may also be prepared by heating phosphorus with a solution of sulphide of barium, when free hydrogen with phosphuretted and sulphuretted hydrogen escape; the last traces of sulphide of barium are removed by the addition of a little sulphate of lead. Hypophosphorous acid forms an uncrystallizable syrup, which has a sour, bitterish taste; its acid properties are but feebly marked, and its solution gradually absorbs oxygen from the air. When heated, it first loses water; and by a stronger heat it is decomposed, emitting phosphuretted hydrogen, whilst phosphoric acid is set free, $2\,(HO, PH_2O_3)$ becoming $(3\,HO,PO_5)+H_3P$. Owing to the partial decomposition of the phosphuretted hydrogen, a little phosphorus

is generally deposited at the same time, and a corresponding quantity of hydrogen is liberated.

Hypophosphites.—The researches of Dulong, of Rose, and of Wurtz have shown that all the hypophosphites retain 2 atoms of water, which are essential to their composition; the acid requires one atom of base for its saturation. Hypophosphite of lead for example, may be represented as PbO,PH_2O_3. They correspond therefore to the monobasic phosphates, but 2 atoms of hydrogen have taken the place of 2 atoms of oxygen in the phosphoric acid. The hypophosphites are all soluble in water; many of them crystallize easily, by spontaneous evaporation; the crystallized salts may be preserved unchanged, but their solutions, when evaporated at a high temperature, are gradually converted into phosphites by absorption of oxygen. Like phosphorous acid they reduce gold and silver from their salts. The hypophosphites of the alkalies contain no water of crystallization: they are deliquescent, and also soluble in alcohol.* The hypophosphite of lime (CaO,PH_2O_3) requires about 6 parts of cold water for solution, and is scarcely more soluble in boiling water. Each atom of the baryta salt retains an atom of water when crystallized at ordinary temperatures, but if crystallized from a boiling solution is deposited in anhydrous tables (BaO,PH_2O_3). The hypophosphite of magnesia ($MgO,PH_2O_3+6\ Aq$) crystallizes in brilliant, regular octohedra, which are efflorescent. The hypophosphites of nickel, cobalt, and protoxide of iron, also retain 6 Aq, those of zinc and manganese retain but 1 atom of water of crystallization, which they lose at 300°.

Hypophosphorous acid is distinguished from phosphorous acid by a remarkable reaction with the salts of copper; if to an excess of free hypophosphorous acid a solution of sulphate of copper be added, and the liquid be warmed to about 130°, a solid insoluble hydride of copper (Cu_2H) is precipitated. On raising the liquid which contains the precipitate, to the boiling point, this hydride is decomposed into hydrogen gas and metallic copper.

(375) Oxide of Phosphorus (P_2O).—A still lower degree of oxidation of phosphorus exists, which possesses neither acid nor alkaline properties. It is always formed in small quantity when phosphorus is burned in air, and is one of the constituents of the red residue after the combustion has terminated. It is not, however, a compound of any importance. Oxide of phosphorus has neither smell nor taste, and is quite insoluble in water.

* Hypophosphite of soda, which is now prepared largely for medicinal purposes, sometimes explodes spontaneously during the evaporation of its aqueous solution.

(376) PHOSPHIDES OF HYDROGEN.—None of the compounds of phosphorus with hydrogen are possessed of acid characters: they are three in number: viz. H_3P; H_2P, and HP_2. The first is gaseous, the second liquid, and the third solid, at ordinary temperatures.

Phosphuretted Hydrogen Gas ($H_3P=34$); *Sp. Gr.* 1·185; *Comb. Vol.* 4.—Phosphuretted hydrogen is a highly inflammable colourless gas, with a fœtid alliaceous odour; it is slightly soluble in water; when transmitted through solution of certain metallic salts such as those of lead, copper, or mercury, it is absorbed and decomposed; phosphides of the metals are produced and are precipitated. Those of lead and copper are black, that of mercury is yellow. Solutions of the salts of gold and silver are reduced to the metallic state, and phosphoric acid is found in solution. When the gas is pure it is wholly absorbed by a solution of chloride of lime. A mixture of the gas with air or with oxygen explodes at a temperature of 300°, or sometimes even at common temperatures, if the pressure be suddenly diminished. In this gas 1 volume of the vapour of phosphorus and 6 volumes of hydrogen are condensed into the space of 4 volumes. Its composition may therefore be thus represented:—

			By weight.		By vol.		Sp. gr.
Phosphorus . . .	P	=	31 or	91·18	1 or	0·25	= 1·071
Hydrogen . . .	H_3	=	3	8·82	6	1·5	= 0·104
Phosphuretted Hydrogen	H_3P	=	34	100·00	4	1·0	= 1·175

The combining volume of phosphuretted hydrogen is the same as that of ammonia, to which it is analogous in composition; but it does not exhibit any marked alkaline properties. Some indication of a basic character is, however, shown by it, for it combines with certain of the acids in definite proportions. For example, its compound with hydriodic acid (H_3P,HI) is formed by the union of equal volumes of the two gases, which in the act of combination do not undergo condensation, for its vapour, according to Bineau, has a density of 2·77; it crystallizes in cubes, which fuse at a moderate heat, and if air be excluded it may be sublimed without alteration. These crystals are deliquescent, and are decomposed by water into hydriodic acid and phosphuretted hydrogen gas. This compound is easily prepared by introducing into a small retort 127 parts of dry iodine ground up with powdered glass, and 31 parts of phosphorus in small fragments; then adding 20 parts of water; the vapours which come off consist of this compound mixed with an excess of hydriodic acid; the hydriodate of phosphuretted hydrogen is condensed in crystals in the neck of the retort, if it

be kept cool. A similar compound may be obtained with hydrobromic acid. Hofmann and Cahours have shown that by displacing the hydrogen in gaseous phosphide of hydrogen, by ethyl and other analogous hydrocarbons, compounds may be obtained which neutralize acids, and are powerfully basic (1029).

Phosphuretted hydrogen combines with the perchlorides of many of the metals, such as those of tin, titanium, antimony, and iron. These compounds are decomposed by water with escape of phosphuretted hydrogen gas.

Preparation.—Phosphuretted hydrogen gas may be obtained in a state of purity by the decomposition of hydrated phosphorous acid by heat; 4 (2 HO,PHO_4) yielding 3 (3 HO,PO_5) + H_3P.

This gas, however, is generally prepared by heating fragments of phosphorus with a strong solution of hydrate of potash, or with cream of lime; hypophosphite of the base is formed, with extrication of phosphuretted hydrogen; $P_4 + 6\ HO + 3\ (KO,HO)$ becoming 3 $(KO, PH_2O_3) + H_3P$. The gas so obtained has the remarkable property of taking fire spontaneously in atmospheric air or in oxygen gas: if allowed to escape into the air in bubbles, each bubble as it breaks produces a beautiful white wreath of phosphoric acid, composed of a number of ringlets revolving in vertical planes around the axis of the wreath itself, as it ascends; thus tracing before the eye, with admirable distinctness, the rapid gyratory movements communicated to the superincumbent air by the bursting of a bubble upon the surface of a still sheet of water. If the bubbles be allowed to rise into a jar of oxygen, a brilliant flash of light, attended with a slight concussion, accompanies the bursting of each bubble. Owing to the spontaneous inflammation of the gas it should be made in small vessels containing but little atmospheric air. Graham has shown that the addition of small quantities of the vapour of some inflammable bodies, such as ether, naphtha, and oil of turpentine, destroys this self-lighting power, and that of porous bodies, such as charcoal, also removes it. On the other hand, the gas obtained from phosphorous acid is not self-lighting, but the addition of so small a quantity as $\frac{1}{10,000}$th of its bulk of nitrous acid gas confers this property upon it.

(377) *Liquid Phosphide of Hydrogen,* H_2P, or $H_{10}P_5$.—The singular property which phosphuretted hydrogen possesses, in certain cases, of igniting spontaneously when mixed with free oxygen, long remained without explanation, as a careful analysis indicated little or no difference in composition between self-lighting gas and the other variety, which does not possess this property. The true cause of the phenomenon was, however, traced a few years ago by

P. Thénard, to the presence of a minute quantity of the vapour of another phosphide of hydrogen ($H_{10}P_5$), which takes fire the instant that uncombined oxygen is presented to it (*Ann. de Chimie*, III. xiv. 5). This compound exists at ordinary temperatures as a volatile liquid, which by exposure to light is decomposed into a yellow, solid, and but slightly inflammable phosphide (HP_2), and into the non-self-lighting gas (H_3P); for $H_{10}P_5 = HP_2 + 3\ H_3P$. It had long been remarked, although analysis showed no difference between the self-lighting and the common gas, that when the former was exposed to sunlight for a few hours, a solid yellow compound was deposited in small quantity upon the sides of the vessel, whilst the gas lost its self-lighting power; and that this power was also destroyed by exposing the gas to a great degree of cold. This effect is evidently due, in the case of the exposure to sunlight, to decomposition of the inflammable compound, and in the case of the application of cold, to its condensation into the liquid form.

Liquid phosphide of hydrogen may be prepared by conducting the gas which is disengaged by the action of water upon phosphide of calcium (Ca_2P), through a bent tube immersed in a freezing mixture of ice and salt; a colourless liquid of high refracting power is thus condensed. It takes fire the instant that it comes into contact with air, and burns with the intense white light of phosphorus. Solar light quickly decomposes it into the solid phosphide (HP_2) and into the gaseous phosphuretted hydrogen. If a little of the vapour of this liquid be allowed to diffuse itself through hydrogen, carbonic oxide, or any other combustible gas, it confers upon it the property of taking fire spontaneously when mixed with atmospheric air or with oxygen.

(378) *Solid Phosphide of Hydrogen* (HP_2).—The liquid phosphide is immediately decomposed by hydrochloric acid; and the solid yellow phosphide of hydrogen is formed. This substance is readily prepared by treating phosphide of calcium (538) with hot hydrochloric acid. It is insoluble in water and in alcohol. When heated with potash the compound is dissolved, and phosphuretted hydrogen gas is liberated. There appear to be two varieties of the solid phosphide, one of a yellow, the other of a green colour; they do not differ from each other in composition. The solid yellow hydride of phosphorus takes fire at about 300°.

(379) Chlorides of Phosphorus.—With chlorine phosphorus forms two compounds, a terchloride, PCl_3, corresponding to phosphorous acid, and a pentachloride, PCl_5, which corresponds to phosphoric acid. So strong is the affinity between these elements, that

in an atmosphere of chlorine phosphorus immediately takes fire. The following table shows the composition of these chlorides, and of two of their derivatives:—

		In 100 parts.			
		Phosph.	Chlorine.	Oxygen.	Sulphur.
Terchloride of phosphorus	$PCl_3 = 137 \cdot 5$	22·54	77·46		
Pentachloride of ditto .	$PCl_5 = 208 \cdot 5$	14·86	85·14		
Oxychloride	$PO_2Cl_3 = 153 \cdot 5$	20·19	69·38	10·43	
Sulphochloride	$PS_2Cl_3 = 169 \cdot 5$	18·28	62·84		18·88

Terchloride of Phosphorus ($PCl_3 = 137 \cdot 5$): *Sp. Gr. of Vapour,* 4·875; *of Liquid,* 1·616 *at* 32°; *Boil. Pt.* 173°·4; *Comb. Vol.* 4.—This liquid is sometimes prepared by causing the vapour of phosphorus to pass over corrosive sublimate placed in a long tube, and gently heated; but it may be obtained more easily and abundantly by transmitting a gentle stream of perfectly dry chlorine gas through dry and melted phosphorus contained in a retort; the operation may be conducted in the same manner as in the preparation of chloride of sulphur (fig. 287); the chloride distils as a very volatile, transparent, colourless, fuming liquid. It dissolves phosphorus freely, and is itself soluble in benzol and in bisulphide of carbon; alcohol and ether decompose it with evolution of great heat, giving rise to various new compounds. It is also immediately decomposed by a large excess of water, and forms phosphorous and hydrochloric acids; $PCl_3 + 6\,HO$ yielding $2\,HO, PHO_3 + 3\,HCl$.

Pentachloride or *Perchloride of Phosphorus* ($PCl_5 = 208 \cdot 5$); *Sp. Gr. of Vapour at* 504°, 3·68; *Comb. Vol.* 8.—This compound is obtained by placing dry phosphorus in a flask provided with a stopcock, exhausting the air, and allowing chlorine to enter so long as it is absorbed; or it may be formed by treating terchloride of phosphorus in a tall glass with an excess of chlorine: it forms a white crystalline solid, which volatilizes below 212° whilst still solid, but it may be fused under pressure. In the flame of a lamp it burns, producing chlorine and phosphoric acid: with ammonia it combines readily. It is very deliquescent, and by a large excess of water is immediately decomposed into phosphoric and hydrochloric acids; $PCl_5 + 8HO$ forming $3\,HO, PO_5 + 5\,HCl$.

Oxychloride of Phosphorus ($PO_2Cl_3 = 153 \cdot 5$); *Sp. Gr. of Liquid,* 1·7; *of Vapour,* 5·40, *Boiling Pt.* 230°; *Comb. Vol.* 4.—This compound is formed when the vapour of water is allowed to mingle slowly with that of the pentachloride, hydrochloric acid and oxychloride of phosphorus being the result. The reaction is as follows: $PCl_5 + 2HO = PO_2Cl_3 + 2HCl$. The oxychloride is a limpid,

volatile, fuming liquid, which is decomposed by the further addition of water into phosphoric and hydrochloric acids.

Oxychloride of phosphorus may be obtained with facility by Gerhardt's plan of distilling 1 part of crystallized boracic acid with 4½ parts of pentachloride of phosphorus, when the following reaction occurs: $3\,PCl_5+2(3\,HO,BO_3)=3\,PO_2Cl_3+6\,HCl+2\,BO_3$. The oxychloride is readily condensed whilst hydrochloric acid passes off in the form of gas, leaving anhydrous boracic acid in the retort. Crystallized oxalic acid may be substituted for boracic acid in this operation, but it does not answer quite so well.

Both the chlorides and the oxychloride of phosphorus have been extensively used in the preparation of various organic substitution-products, particularly the oxychlorides and anhydrides of the organic acids (1097, 1099).

Sulphochloride of Phosphorus ($PS_2Cl_3=169{\cdot}5$; *Boiling Pt.* 257°) is a compound corresponding to the oxychloride, but containing sulphur instead of oxygen. It is obtained by decomposing pentachloride of phosphorus with sulphuretted hydrogen: $PCl_5+2\,HS$ yielding $PS_2Cl_3+2\,HCl$. It is a fuming, colourless liquid, which, if heated with a solution of caustic soda in excess, exchanges its chlorine for oxygen; chloride of sodium is formed, and a *sulphoxyphosphate of soda* may be obtained in six-sided tabular crystals which contain 24 equivalents of water. The composition of this salt is analogous to that of the tribasic phosphate of soda, but the two are not isomorphous. The following equation explains the changes which accompany its production (Wurtz):—

$$PS_2Cl_3+6\,(HO,NaO) = 3\,NaO,PS_2O_3+3\,NaCl+6\,HO.$$

One half of the soda is decomposed, imparting its oxygen to the sulphochloride, from which it receives a corresponding amount of chlorine.

(379 *a*) Bromides of Phosphorus.—*A Terbromide* (*Sp. Gr.* at 32°, 2·925; *Boiling Pt.* 347°·5), *Pentabromide*, and *Oxybromide* of phosphorus, analogous to the corresponding compounds with chlorine, may be formed by similar methods.

(380) Iodides of Phosphorus.—Two iodides of phosphorus may be formed, viz., a biniodide and a teriodide (Corenwinder, *Ann. de Chimie*, III. xxx. 242). *The Biniodide* ($PI_2=285$) may be obtained by dissolving 1 part (or 1 atom) of phosphorus in bisulphide of carbon and adding 8¼ parts (or 2 atoms) of iodine: by cooling the mixture artificially, thin flexible prismatic crystals of the iodide are deposited, of a bright orange colour. It melts at

230°, and is decomposed by water, hydriodic acid being one of the products.

Teriodide of Phosphorus ($PI_3=412$).—This compound may be obtained in a similar manner to the last, by dissolving 1 part of phosphorus and 12½ parts of iodine in bisulphide of carbon; the liquid is concentrated by evaporation, and on cooling it by a freezing mixture, dark red six-sided plates are formed; it melts between 120° and 130°, and on cooling crystallizes in fine prisms. It deliquesces rapidly when exposed to the air.

Brodie (*Q. J. Chem. Soc.*, v. 289) finds that iodine, when heated with phosphorus in the proportion of 1 atom of iodine to 100 atoms of phosphorus, converts nearly the whole of the phosphorus into the red variety described by Schrötter. When phosphorus was placed in a long tube, and heated till it just melted, and iodine was projected gradually into the phosphorus, the iodine was dissolved, colouring the phosphorus slightly red; when heated by an oil-bath to 212°, the colour became deep red; and between 250° and 266°, a scarlet powder was deposited on the sides of the tube; at 284° the mass was quite solid, and on raising the heat to 392° F., a sharp explosion took place: a sudden evolution of heat occurred, and the cork which closed the tube was blown out by the vapour of phosphorus. The red mass may be distilled in closed tubes, and when it is condensed in the cooler portions of the tubes it is still in the red modification. The changes which occur in the process are supposed to be the following; first, the formation of biniodide of phosphorus, next the transformation of this iodide by heat into an allotropic iodide, and thirdly, the decomposition of this new iodide into red phosphorus and a volatile iodide, which acts upon a further portion of the phosphorus; and thus the action is indefinitely continued.

(381) Phosphamide (HN_2P).—If terchloride of phosphorus be cooled by a freezing mixture, and saturated with ammoniacal gas, a white saline mass ($5\ H_3N,PCl_3$) is obtained; it is to be introduced into a tube of Bohemian glass, and heated to redness in a current of dry carbonic acid as long as any sal ammoniac is sublimed: a yellowish-white bulky amorphous powder remains behind: this substance is Rose's *phosphide of nitrogen*. In closed vessels it sustains a red heat without fusion or volatilization, but when heated in air it is slowly oxidized, with formation of phosphoric acid; if projected into fused hydrate of potash, it is decomposed with incandescence, phosphate of potash being formed, whilst ammonia and nitrogen are disengaged: but it is remarkable that dry chlorine and hydrochloric acid gases, and the vapour

of sulphur, are without action upon it, even at red heat; and it is but very slowly attacked by concentrated nitric acid. Solutions of the alkalies exert scarcely any action upon it. When heated in hydrogen, ammonia is formed. It combines with sulphuretted hydrogen, and if heated in a current of this gas the new compound as it is formed is slowly sublimed in the form of a white powder. There can be no doubt, however, that, as stated by Gerhardt, the so-called phosphide of nitrogen contains hydrogen, and is in reality phosphamide, (HN_2P).

(382) SULPHIDES OF PHOSPHORUS.—Sulphur and phosphorus may be melted together in all proportions: several definite compounds exist between them, corresponding in composition with the oxides of phosphorus; and in addition to these, a combination, PS_{12}, may be formed (Berzelius). All the sulphides of phosphorus are more fusible than either element separately, and are exceedingly inflammable: most of them may be obtained in crystals. They combine with the sulphides of the alkaline metals, and form a series of definite salts. The combination of sulphur with phosphorus should be gradually effected under warm water; great heat is extricated by their union, and the experiment requires to be conducted very carefully, in order to avoid explosion.

CHAPTER VIII.

SILICON AND BORON.

§ I. SILICON, OR SILICIUM ($Si = 14$).*

Theoretical Density of Vapour ($Si = 2$ vols.), 0·9674.

(382 *a*) *Analogies of the Silicon Group.*—Silicon presents a certain analogy with boron in its tendency to unite with fluorine and with nitrogen: but its relationship to niobium and tantalum is still more strongly marked, not only in these particulars, but in its tendency to form an acid with 2 atoms of oxygen, and its production of a volatile liquid bichloride. Silicon likewise exhibits a similar resemblance to titanium and tin. These metals might probably be arranged thus in a series parallel with niobium and tantalum:—

* It would be consistent with analogy if the atomic weight of carbon be represented as $C = 12$, and $O = 16$, in accordance with Gerhardt's notation, to indicate that of silicon as $Si = 28$, in which case silicic acid would be $SiO_2 = 60$.

	Silicon.	
Niobium		Titanium
Tantalum		Tin.

(383) SILICON when in combination with oxygen is the most abundant solid component of the earth's crust. It is the essential constituent of *Silex* or flint, and hence the origin of the term silicon. In order to obtain the element in its uncombined form, a mixture of fluor-spar with fine quartzose sand or ground flints is heated with concentrated sulphuric acid; a gaseous fluoride of silicon is formed, which is partially soluble in water, producing an acid solution. This acid liquid, when neutralized with a solution of potash, yields a sparingly soluble salt (KF,SiF_2). This silico-fluoride of potassium is to be thoroughly dried, and mixed in a glass or iron tube with eight or nine-tenths of its weight of potassium, and heated. Fluoride of potassium is formed, whilst silicon is reduced and partially combined with the excess of potassium; (KF,SiF_2) + 2 K = 2 Si + 3 KF. The mass, when cold, is treated with cold water, which produces a copious extrication of hydrogen gas, owing to the decomposition of the water by the excess of potassium. The washing with cold water is continued as long as any alkaline reaction upon test paper is observed; when this ceases, it may finally be well washed with boiling water, so long as anything is dissolved. Sodium may be advantageously substituted for potassium in this experiment, in the proportion of 1 part of sodium to 2 of the silicofluoride. Silicon may also be obtained by heating potassium or sodium placed in porcelain trays, in a glass tube lined with mica, and exposed to a current of the vapour of chloride of silicon.

Silicon may be obtainedi n three distinct modifications: viz., the *amorphous*, Si_γ, the *graphitoid*, Si_β, and the *crystalline*, Si_α, modification.

1. *Amorphous Silicon*, Si_γ.—When procured by the processes above described, silicon presents the appearance of a dull brown powder, insoluble in water, in which it sinks. It is a non-conductor of electricity; it soils the fingers when touched; it is not acted upon by nitric or sulphuric acid, but is readily soluble in hydrofluoric acid, and in a warm solution of potash. When heated in air or in oxygen it burns brilliantly, and is converted into silica, which fuses from the intense heat emitted, and forms a superficial coating over the unburnt silicon.

2. *Graphitoid Silicon*, Si_β.—The brown powder just described, if heated intensely in a closed platinum crucible, parts with a trace

of hydrogen, shrinks greatly, becomes much denser and darker in colour, and undergoes a remarkable change in properties. After such ignition, the silicon may be heated strongly in air or in oxygen, even when urged in the blowpipe flame, without taking fire; it has become sufficiently heavy to sink in oil of vitriol, and it resists the action of pure hydrofluoric acid, although if treated with a mixture of nitric and hydrofluoric acids it is rapidly dissolved. It may even be fused with nitre or with chlorate of potash without undergoing oxidation; but if the heat be urged to whiteness, the silicon burns brilliantly in the nitre; the oxidation, however, is much hastened by the addition of a little carbonate of potash; the mixture then deflagrates briskly, even though it may be at a much lower temperature: by fusion with carbonate of potash alone, silicon is easily and completely oxidized; in both cases, silica is formed, and is immediately dissolved by the melted alkali. The properties of this compact form of silicon much resemble the graphitoid modification described by Deville and by Wöhler, who obtained the silicon in hexagonal plates, by treating an alloy of silicon and aluminum with hydrochloric acid,* the silicon remains behind in the form of hexagonal plates, which have a sp. gr. of 2·49,† and a metallic lustre. In this form it is a conductor of electricity; it may be heated to whiteness in a current of oxygen without undergoing change, but it is gradually dissolved by a mixture of hydrofluoric and nitric acid, though it is oxidized but very slowly when fused with hydrate of potash. When heated in a current of hydrochloric acid, a volatile liquid, the hydrochlorate of protochloride of silicon, (2 HCl, 3 SiCl) is formed (388 *a*), whilst hydrogen gas is liberated.

3. *Crystalline Silicon*, Si_a.—According to Deville (*Ann. de Chimie*, III. xlix. 65), silicon requires for its fusion a temperature between the melting point of cast iron and that of steel. In order to fuse it, he introduces the silicon into a platinum crucible lined with lime and protected by an outer clay crucible: the whole is then intensely heated in a wind furnace. If the lining of lime cracks, and the silicon reaches the platinum, the crucible is spoiled, owing to the formation of a silicide of platinum. Fused silicon may also be procured when the mixture of chloride of sodium with reduced silicon, obtained by igniting sodium in the vapour of chloride of silicon, is placed in a crucible lined with charcoal, and exposed to intense heat in a forge; the chloride of sodium becomes

* Silicon appears to have the same sort of tendency to combine with aluminum that carbon has to unite with iron.

† I found a sample of graphitoid silicon to possess a sp. gr. of 2·337.

volatilized, and the silicon is fused into globules in the midst of the melted glass. These globules frequently show well-marked indications of crystallization in forms probably belonging to the prismatic system; they have a dark steel-grey colour, and a lustre like that of specular iron ore: now and then the silicon is found crystallized in regular double six-sided pyramids. It may also be obtained in regular six-sided prisms terminated by three-sided pyramids, derived from the octohedron, by exposing pure aluminum in porcelain trays, heated intensely in a porcelain tube, to a current of the vapour of chloride of silicon: the aluminum is volatilized as chloride of aluminum, leaving the silicon in crystals which have a reddish lustre; they are hard enough even to cut glass like the diamond. Crystals of silicon may likewise be procured, and with less difficulty, by heating an earthen crucible to redness, and introducing a mixture of 3 parts of silicofluoride of potassium with 1 part of sodium, cut into small pieces, and 1 of granulated zinc. The mixture must be maintained at a red heat, but below the temperature necessary to volatilize the zinc, until the slag is completely melted: it must then be allowed to cool slowly. The mass of zinc thus obtained contains long needles of silicon formed of rhombic (?) octohedra, inserted one into the other: the adhering zinc may be removed by digestion, first in hydrochloric, and afterwards in boiling nitric acid. If a very high temperature be employed in this operation the whole of the zinc may be expelled, and the silicon obtained in the fused condition.

Silicon forms two oxides; one, which is of recent discovery, and is only known in the hydrated state; the other is the well-known compound, silica, or silicic acid.

		In 100 parts.		
		Silicon.	Oxygen.	Water.
Hydrated oxide of silicon,	$2HO, 3SiO = 84$	50·00	28·58	21·42
Silicic acid	$SiO_2 = 30$	46·66	53·34	

(384) Silicic Acid or *Silica*, (SiO_2 = 30), *Sp. Gr.* 2·642.—Much difficulty has been experienced in deciding on the number of proportionals of oxygen that this compound contains. Berzelius represented it as a teroxide. There are, however, reasons which render it more probable that it contains only 2 atoms of oxygen, and that it corresponds in composition to carbonic acid: for example, one atom of chloride of silicon, when converted into vapour, instead of forming an exception to the general rule, as it does upon the theory of Berzelius, would then produce 2 volumes of vapour as usual: and in decomposing fused carbonate of potash by the addition of finely divided silica, it is found that the whole

of the carbonic acid is expelled when the proportion of silica is to the carbonate as 30 to 69.* Gmelin has calculated the formulæ of the natural silicates upon this supposition, and his formulæ have been adopted by Brooke and Miller in their treatise on Mineralogy. This view has the advantage of greater simplicity, and it will be employed in this work. According to the experiments of Dumas, 100 parts of silica contain 46·7 of silicon, and 54·3 of oxygen.

Pure silica occurs in rock crystal and in some forms of quartz, crystallized in six-sided prisms, transversely striated, and terminated by six-sided pyramids. It is nearly pure in agate, flint, calcedony, and opal; it constitutes the principal ingredient of all sandstones; and it enters largely into the composition of felspar, and a vast variety of minerals. Pure silica is perfectly transparent and colourless; in hardness it approaches the precious gems. A heat as intense as that of the oxyhydrogen blowpipe is required for its fusion; it then melts to a transparent glass, which may be drawn out into fine, flexible, elastic threads. Native silica is insoluble in water, and in all acids except the hydrofluoric. It is not volatile when heated alone, but when heated in a current of steam it undergoes partial sublimation, and is thus frequently found in the throats of furnaces, forming concretionary nodules, somewhat resembling calcedony in appearance.

Preparation.—Silica presents the characters of an earth, but though insoluble it possesses feebly acid properties, as is shown by the usual process of obtaining it in a state of purity:—A mixture of carbonate of potash and soda is fused by a red heat, and one-third of its weight of ground flint, or some other siliceous mineral in fine powder, is added in small quantities to the melted mass; on each addition a brisk effervescence, due to the escape of carbonic acid, takes place; the mixture is then heated strongly for some minutes. It is afterwards allowed to cool, and if digested in water the mass is slowly dissolved, with the exception of a portion of the impurities, such as oxide of iron and titanic acid, which the siliceous material may have contained. A larger quantity of silica than that above indicated would stillyield a mixture which might be fused by a strong heat; but it becomes less soluble in proportion to the excess of silica, till at length a point is reached at which it is no longer soluble in water or in the com-

* The experiments of Colonel Yorke (*Phil. Trans.*, 1857) have, however, shown that the proportion of carbonic acid expelled by equal weights of silica from an excess of the different carbonates, varies with the nature of the base; carbonate of soda losing a larger proportion than carbonate of potash, and carbonate of lithia more than carbonate of soda, where equal quantities of silica were employed.

mon acids; indeed, it forms the basis of glass. When it is proposed to obtain pure silica, however, an excess of alkali is always used; the resulting compound is then easily attacked by acids, in which it is wholly dissolved, if the acid be dilute and in sufficient quantity. If the solution in hydrochloric acid be evaporated, the silica is separated as a gelatinous hydrate, which, by continuing the heat, is converted into a white earthy powder no longer soluble in acids: after being digested with oil of vitriol to remove traces of titanic acid, and decanting the strong acid, it must be well washed as long as anything is dissolved; if then dried and ignited, it is perfectly pure.

As thus procured, silica, like charcoal and other porous bodies, rapidly absorbs aqueous vapour from the air, without becoming sensibly moist. Whilst in this extreme state of subdivision, its particles, when heated, exhibit a singular mobility; they flow almost like a liquid when the crucible containing them is inclined, and they are scattered by the least breath of air.

Perfectly pure silica may also be procured by transmitting the gaseous fluoride of silicon into water; a partial decomposition of the gas occurs, and one third of its silicon is oxidized and deposited in white flocculi, which, if washed and ignited, furnish silica of snowy whiteness; $3\ SiF_2 + 2\ HO$, yielding $SiO_2 + 2\ (HF,SiF_2)$. Silica may likewise be obtained nearly pure by heating colourless quartz to redness, and quenching it in water; the mineral is rendered friable by this treatment, and is then easily reduced to a fine powder: common flints treated in a similar manner give a very white powder, which is nearly pure silica.

(385) *Hydrates of Silica.*—Insoluble, however, as silica generally is in water, a modification of it exists which may be dissolved completely, though in small quantity. When dissolved, it furnishes a tasteless solution, which does not redden litmus; and when evaporated at a gentle heat, the solution leaves a semi-transparent mass, which by further desiccation crumbles to a white powder. This white powder is generally stated to be soluble in dilute acids; but Doveri (*Ann. de Chimie,* III. xxi. 41) considers that this is an error, arising from the perfect transparency which the hydrate of silica assumes when treated with dilute acids. If the solution be filtered, nearly the whole of the silica remains on the filter in the form of a transparent jelly. Silica, in fact, when once deposited, even in the gelatinous form, is almost insoluble either in water or in acids; but in certain cases the silica is dissolved at the moment of its liberation from some of its compounds which are already in solution. For instance, if a dilute solution

of an alkaline silicate be poured into a considerable excess of hydrochloric acid, the whole of the silica is retained in solution: but it may be precipitated from this acid solution by the gradual addition of potash, so as to neutralize the acid: and if to a solution of an alkaline silicate in water hydrochloric acid be added gradually, the silica is precipitated in a gelatinous form in proportion as the alkali is neutralized.

There is considerable difficulty in obtaining a definite hydrate of silica, as it easily loses a portion of its water at low temperatures, and is moreover a very hygroscopic substance. Ebelmen, by the action of moist air upon silicic ether, obtained a transparent, glassy hydrate, which had a composition represented by the formula, $3\,HO, 2\,SiO_2$; and a compound which gave similar results on analysis was procured by Doveri on drying the ordinary gelatinous hydrate of silica *in vacuo* over sulphuric acid without the aid of heat. Fuchs obtained two hydrates of silica, one containing from 9·1 to 9·6 per cent. of water, corresponding to the formula $3\,SiO_2,HO$, which requires 9·1 per cent., the other between 6·6 and 7 per cent., agreeing nearly with the formula $4\,SiO_2,HO$, which would contain 6·9 per cent. of water.

A very white and light hydrate of silica occurs naturally in abundance in beds situated at the base of the chalk formation, between the upper greensand and the gault: the proportion of hydrated silica in these deposits varies very greatly, ranging from 5 to as much as 72 per cent., being most abundant in the upper portion of the deposit (Way). A mixture of this material with slaked lime, when made into a paste with water, is, in a few weeks, converted into a silicate of lime, and the change is accelerated by the presence of 2 or 3 per cent. of soda.

Insoluble silica may be gradually converted into the soluble variety by long digestion with solutions of the alkalies. Even flints in their unground condition may be dissolved in strong solutions of caustic alkali, if the solution be digested upon them under pressure at a temperature of between 300° and 400°. The very concentrated solution of silicate of potash or of soda of glairy consistence which may thus be formed, has been used by Mr. F. Ransome, of Ipswich, as a cement for consolidating siliceous sand into an artificial stone:—finely divided siliceous sand, mixed with suitable colouring material, is moistened with this cement, and pressed into moulds; after gradual drying the mass is fired: at a high temperature the silicate becomes semi-vitrified, and agglutinates the grains of sand; a very hard, durable, artificial sandstone, which previous to being fired can be moulded into any desired

form, is thus obtained. Finely divided hydrate of silica is also dissolved by the alkaline carbonates: the carbonates are only partially decomposed by the silica which is dissolved. It appears to be owing to the solubility of silica in solutions of the carbonates that almost all spring and river waters contain silica in solution in minute quantity; on evaporation the silica is obtained in the insoluble form. When the action of the alkaline liquid is aided by that of a high temperature, as is the case with the Geysers or boiling springs of Iceland, very large quantities of silica are dissolved, which, as the liquid cools, are deposited as 'petrifactions' on surrounding objects exposed in the basin or in the stream.

Silica also exists in the soluble form in a class of minerals termed zeolites, which are hydrated siliceous compounds (571) found in the cavities of the amygdaloid rocks. The zeolites, if finely powdered, and treated with hydrochloric acid, swell up to a transparent jelly; this gelatinous mass is the hydrate of silica.

These observations on the various conditions under which silica may be rendered soluble derive their interest from the extensive formation of crystallized silica, so abundantly diffused over the surface of the earth. The zeolites may have been obtained by deposition from solution; calcedony possibly by spurious sublimation; quartz and agate by crystallization from an aqueous solution.

(386) *Silicates.*—The silicates are most abundant natural productions. All the forms of clay, felspar, mica, hornblende, and a large number of other common minerals, are compounds of this description.

Silica combines with bases in several different proportions; most of its compounds are found in the form of crystallized minerals, many of which are double silicates of very complex composition. The combinations with bases which are of most usual occurrence belong to one or other of the following classes:—

		Examples.	Formulæ.
$2\,MO, 3\,SiO_2$, or	Sesquisilicates	Silicate of lime	$2CaO, 3SiO_2$
		Meerschaum, (hydrated silicate of magnesia)	$2\,MgO, 3\,SiO_2 + 2\,HO$
MO, SiO_2	Neutral silicates	Wollastonite, (silicate of lime)	CaO, SiO_2
		Dioptase, (hydrated silicate of copper)	$CuO, SiO_2 + HO$
$2\,MO, SiO_2$	Dibasic silicates	Olivine	$2\,(Mg, Fe)\,O, SiO_2$
		Iron forge cinder	$2\,FeO, SiO_2$
$MO, 2\,SiO_2$	Bisilicates. The composition of many of the ordinary varieties of glass may be approximatively represented by mixtures of different silicates which have this formula.		

In the above formulæ, MO stands for 1 equivalent of any metallic protoxide, such as lime, magnesia, or protoxide of iron.

Most of the silicates are fusible; their fusibility is increased by mixture with each other; those which contain readily fusible oxides melt at the lowest temperature, and in general the basic silicates fuse more readily than those which are neutral in composition, or which contain excess of acid. All the silicates are insoluble in water, with the exception of silicates of the alkalies which contain a large amount of base. The hydrated silicates, and those which contain the largest proportion of base, are those most easily decomposed by acids; but the anhydrous neutral and acid silicates of the earths are not decomposed by any acid except the hydrofluoric. The silicates may be detected by fusing them with carbonate of soda or of potash, and then heating the residue with acid, and evaporating to dryness; on treating what is left with hot water, the silica remains undissolved in the form of a white powder, which, when fused with carbonate of soda upon platinum foil before the blowpipe, yields a colourless bead of glass. The freedom of silica from bases may be ascertained by its being volatilized without residue when evaporated with pure hydrofluoric acid in excess. Pure silica is not attacked by fusion with microcosmic salt, but is left as a spongy mass in the clear bead; if any earth or base be present, the bead is generally more or less opalescent. Borax dissolves silica slowly, when fused with it, forming a clear colourless bead.

The acid character is so feebly marked in silica, that the ordinary vegetable acids, such as the acetic, the oxalic, and the tartaric, precipitate silica from its combinations with the alkalies; and a current of carbonic acid gas, or even the gradual absorption of carbonic acid from the atmosphere, produces a similar result. At a high temperature, however, the action is reversed; for as silica is not volatilized to any perceptible extent by the heat of a furnace, it decomposes the carbonates and the salts of all the volatile acids when ignited with them; thus even the sulphates yield up their bases to the silica, whilst the sulphuric acid is expelled.

(386*a*) HYDRATED PROTOXIDE OF SILICON ($2\,HO, 3\,SiO$).—When crystallized silicon is heated to barely visible redness in a current of gaseous hydrochloric acid, hydrogen is liberated and a volatile liquid, hydrochlorate of protochloride of silicon ($2\,HCl, 3\,SiCl$) is formed; this compound when mixed with water is immediately decomposed into hydrochloric acid and a voluminous white powder, the hydrated protoxide of silicon; $2\,HCl, 3\,SiCl + 5\,HO$ becoming $2\,HO, 3\,SiO + 5\,HCl$.

This hydrated oxide of silicon at temperatures above 32°, when in contact with water, undergoes oxidation, and evolves hydrogen. Wöhler and Buff (*Ann. de Chimie*, III. lii. 276)

describe this oxide when dry as a snow-white powder, sufficiently light to float upon water, though it sinks in ether. The caustic alkalies and their carbonates dissolve it rapidly with brisk effervescence, owing to the formation of a silicate of the base whilst hydrogen escapes. The acids, with the exception of the hydrofluoric, do not act upon it. It may be heated in air to 570° without alteration; but at a somewhat higher temperature it takes fire, burning with scintillation, and emitting a phosphorescent light, at the same time giving off hydrogen gas, which burns explosively. If heated in a closed crucible it is decomposed into a mixture of silicon and silica; hydride of silicon (386 *b*) being liberated, but undergoing immediate decomposition. Hydrated protoxide of silicon is slightly soluble in water, but the liquid quickly undergoes decomposition, evolving hydrogen gas. The solution exerts a strong reducing power, precipitating gold and palladium from neutral solutions, in a metallic form. It also instantly bleaches a solution of permanganate of potash; and throws down reduced selenium and tellurium, from solutions of selenious and tellurous acids in hydrochloric acid. Wöhler and Buff, however, think it probable that this solution contains a still lower oxide of silicon than the one above described.

The white hydrated protoxide of silicon is best prepared by placing crystallized silicon in a wide glass tube connected with a U-tube cooled by a mixture of ice and salt, whilst the apparatus terminates in a bent tube dipping into ice-cold water; the silicon is to be raised to a barely visible red heat, and a current of dry hydrochloric acid gas transmitted; hydrochlorate of protochloride of silicon is formed, and in part condensed in the U-tube, and the portion which passes on is decomposed by the water. The voluminous white precipitate thus formed consists of the hydrated protoxide of silicon, and is to be quickly pressed between folds of blotting-paper and dried *in vacuo* over sulphuric acid.

(386 *b*) Hydride of Silicon.—Along with the foregoing compound, Wöhler and Buff have also described a remarkable gaseous combination of hydrogen and silicon. It has not been procured in a pure state, but may be obtained mixed with a large quantity of free hydrogen as a spontaneously inflammable gas, when a wire or plate of aluminum contaminated with silicon is placed in a solution of chloride of sodium and made the positive pole of a feeble voltaic battery. A large surface of aluminum and the avoidance of any considerable elevation of temperature are necessary to insure the maximum production of the hydride.

The electrolytic gas is colourless; when allowed to burn in

the air, it emits white fumes, consisting of amorphous silica. If a cold plate of porcelain or of glass be introduced into a jet of the burning gas, a brown film of reduced silicon is deposited upon its surface. It is also decomposed by transmission through a glass tube heated to redness, when a coating of reduced silicon is deposited, and the gas is found to have lost its self-lighting power. Its exact composition is not known. This gas precipitates many metallic solutions, such as sulphate of copper, nitrate of silver and chloride of palladium; but is without action upon the solutions of lead and of platinum; the precipitates in most cases contain silicon.

Hydride of silicon may also be obtained by decomposing with cold diluted hydrochloric acid an impure silicide of magnesium obtained by mixing intimately 40 parts of fused chloride of magnesium, 35 of dried silicofluoride of sodium, and 10 of fused chloride of sodium; these are mixed in a warm dry tube, with 20 parts of sodium in small fragments and thrown into a Hessian crucible, heated to redness, which is immediately covered and heated till the vapours of sodium cease to burn.

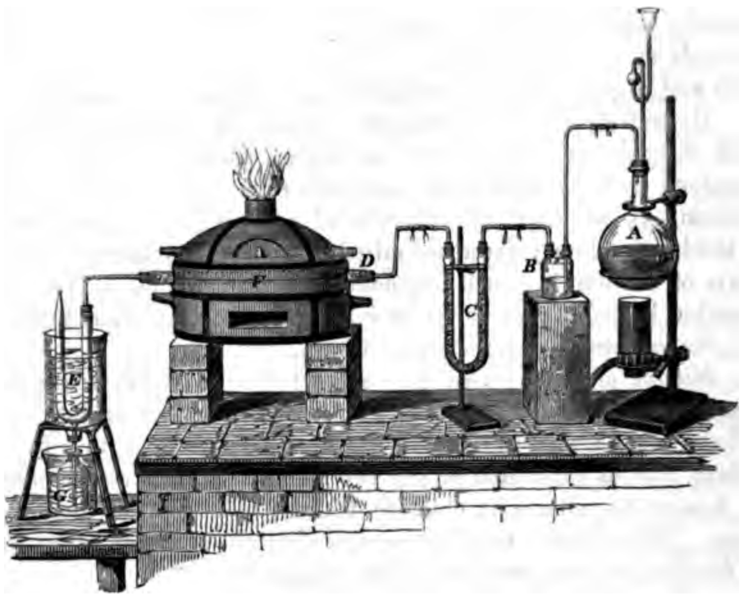
Nitride of Silicon may be obtained by the direct action of nitrogen upon silicon at a very high temperature; crystallized silicon, when heated in nitrogen gas, becoming coated with a light bluish, fibrous compound of the two elements. This nitride may be heated to redness in chlorine without undergoing decomposition. When heated to full redness in a current of steam, ammonia is disengaged abundantly and silica is formed.

(387) Sulphide of Silicon ($SiS_2=46$).—A sulphide corresponding in composition to silicic acid is formed by transmitting the vapour of bisulphide of carbon over a mixture of finely divided silica and carbon: and when either compact or pulverulent silicon is strongly heated in an atmosphere of sulphur, combustion occurs with a red glow, and a white earthy-looking sulphide, which rapidly absorbs moisture from the air, is the result: it is completely soluble in water, but it is decomposed whilst undergoing solution; $SiS_2 + 2\ HO$ becoming $SiO_2 + 2\ HS$; sulphuretted hydrogen and soluble silica being formed: the silica may be obtained as a jelly by evaporation.

(388) Chloride of Silicon ($SiCl_2, =85$).—*Comb. Vol. as Vapour*, 2; *Sp. Gr. of Liquid*, 1·5237 *at* 32°; *of Vapour*, 5·939; *Boiling Pt.* 138°.—This compound may be formed by heating silicon in chlorine, or more economically by the following indirect method. Finely powdered silica is made up into a paste with oil and charcoal, heated in a covered crucible, and the charred mass in fragments is transferred to a porcelain tube, in which it is ignited

and subjected to a current of dry chlorine: neither chlorine nor carbon separately can decompose silica, but together they effect its decomposition easily; carbonic oxide escaping, whilst chloride of silicon is formed; $SiO_2 + Cl_2 + 2C = (CO)_2 + SiCl_2$. The product is received into vessels cooled with a freezing mixture. Fig. 291

FIG. 291.



shows a form of apparatus by which the chloride may be readily prepared: D is a porcelain tube, which contains the mixture of charcoal and silica; chlorine is liberated from the flask, A, washed with water in B, dried by transmitting it over pumice and sulphuric acid contained in the tube C, and allowed to pass through the tube D, which with its contents is exposed to a red heat in the furnace; the chloride of silicon distils over into the bent tube, E, where it is condensed by immersion in a freezing mixture of ice and salt; a tube fused into the bend of the tube E, conveys the chloride into a bottle, G, which may also be kept cool by ice.

Chloride of silicon is a transparent, colourless liquid, with a pungent, acid, irritating odour; it is very volatile, and fumes strongly in the air. Its composition is the following:—

		By weight.		By vol.		Sp. gr.
Chlorine ...	Cl_2 =	71	or 83·53	4	= 2	= 4·906
Silicon ...	Si =	14	16·47	2 ?	= 1	= 0·967
Chloride of silicon	$SiCl_2$ =	85	100·00	2	1	= 5·873

Water immediately decomposes chloride of silicon, depositing rdrated silica, and forming hydrochloric acid. A moist atmohere also decomposes the chloride, causing the deposition of silica opaque lamellar plates, which like the mineral *hydrophane* come transparent when immersed in water, but resume their acity on drying: the siliceous deposit obtained from the joints the bamboo, known as *tabasheer*, exhibits the same peculiarity. ie liquid chloride does not act on potassium, but if the metal be ated in its vapour, chloride of potassium is produced, and silicon set free; this is one of the best methods of obtaining silicon

Two compounds between the sulphide and the chloride of icon have been obtained (Pierre); they may be represented by the rmulæ (SiS_2, 2 $SiCl_2$, *Sp. Gr. of Vapour*, 5·24)* and (2 SiS_2, $SiCl_2$).

Bromide of Silicon ($SiBr_2$) is analogous in properties to the loride: it may be formed in a similar manner.

(388*a*) HYDROCHLORATE OF PROTOCHLORIDE OF SILICON (2HCl, 3SiCl=221·5); *Sp. Gr. of Liquid*, 1·65; *Boiling Pt.* 108°; (Wöhler d Buff, *Annal. de Chimie*, III. lii. 269).—This compound is a lourless, highly mobile liquid, which fumes powerfully on posure to the air, depositing a white film upon surrounding dies, and emitting a vapour of suffocating odour. It is highly lammable, and burns with a greenish, feebly luminous flame, positing silica and emitting hydrochloric acid. If its vapour mixed with oxygen, it explodes violently on the transmission of e electric spark, silica being deposited, whilst hydrochloric acid d chloride of silicon are formed. If passed through a tube ated to redness, it is decomposed into a mixture of chloride of icon and hydrochloric acid, whilst half its silicon is deposited in e form of a brown amorphous crust exhibiting a metallic lustre. ater decomposes it immediately with great elevation of tempeure, hydrated protoxide of silicon and hydrochloric acid being med: (2HCl, 3 SiCl) + 5 HO yielding (2 HO, 3 SiO) + 5 HCl.

The mode of preparing this compound by transmitting dry drochloric acid over crystallized silicon heated to dull redness, s already been described when speaking of the preparation of the drated protoxide of silicon (386 *a*).

* The density of this substance, supposing it to give 6 volumes of vapour, 2 volumes of the vapour of sulphide of silicon, and 4 of chloride of silicon, ited without condensation, is 5·018; for

		By volume.			Sp. gr.
SiS_2	=	2	or 0·33	=	3·959
2 $SiCl_2$	=	4	0·67	=	1·059
		6	1·00		5·018

A similar liquid compound (2 HBr, 3 SiBr; *Sp. Gr.* 2·5) may be obtained in like manner with hydrobromic acid. The corresponding compound of iodine (2 HI, 3 SiI) forms a fusible, crystalline solid.

(389) FLUORIDE OF SILICON ($SiF_2=52$): *Sp. Gr.* 3·60; *Comb. Vol.* 2.—The fluoride is one of the most remarkable compounds of silicon: so powerful is the affinity between fluorine and silicon that hydrofluoric acid separates silicon from its most intimate combinations, such as silicic acid and glass. In order to prepare the fluoride of silicon, equal parts of finely powdered fluor-spar and siliceous sand, or powdered glass, are mixed in a capacious flask or retort, with twelve times their weight of oil of vitriol. On the application of heat, a colourless gas, with a peculiar, pungent, acid odour, is given off; hydrofluoric acid is liberated, and this immediately attacks the silica, as is shown in the following representation of the reaction:—

$$2\ CaF+2\ (HO,SO_3)=2\ HF+2(CaO,SO_3);$$
$$\text{and } 2\ HF+SiO_2=2\ HO+SiF_2.$$

The composition of the gas may be thus represented:—

			By weight.		By volume.			Sp. gr.
Silicon ...	Si	=	14	or 26·9	2	or 1	=	0·967
Fluorine ...	F_2	=	38	73·1	4	2	=	2·620
Fluoride of silicon	SiF_2	=	52	100·0	2	1	=	3·587

Fluoride of silicon fumes strongly in air; it is not inflammable, but extinguishes a lighted taper; under strong pressure it was liquefied by Faraday; and according to Natterer it becomes solid at—220°. The gas is dissolved and partially decomposed by water, it must therefore be collected over mercury, and in jars which have been perfectly dried at a high temperature; the slightest trace of moisture on the surface of the jar causes a deposition of silica, which adheres very firmly to the glass and renders it opalescent. Fluoride of silicon combines with twice its volume of ammoniacal gas, and forms with it a crystalline volatile compound.

(390) SILICOFLUORIC ACID: *Hydrofluosilicic Acid* ($HF, SiF_2=72$).—When a stream of gaseous fluoride of silicon is transmitted through water, it is partially decomposed and partially dissolved. Two atoms of water react on 3 atoms of the fluoride, and produce the silicofluoric acid, which is dissolved, whilst one-third of its silicon is deposited as silicic acid:—

$$3\ SiF_2+2\ HO=SiO_2+2\ (HF,SiF_2).$$

In the preparation of this acid, the tube from which the fluoride is escaping must not plunge at once into water, otherwise it will

speedily become obstructed by the deposited silica. This inconvenience may be prevented by placing a little mercury at the bottom of the vessel, in order that the tube may dip beneath the mercury, as shown in fig. 292. Each bubble as it rises becomes surrounded by a siliceous envelope, and finally the liquid sets into a gelatinous mass: the acid liquid is separated by pressure in linen from the deposit, which when freed from adhering acid, constitutes a pure hydrate of silica.

FIG. 292.

A saturated solution of silicofluoric acid forms a very sour, fuming liquid. In solution it does not attack glass; but it does so if allowed to evaporate upon it; the fluoride of silicon becomes volatilized, leaving free hydrofluoric acid, which, reacting on the silica, produces water and fluoride of silicon, as in the ordinary process for making that gas; $2\ HF + SiO_2 = 2\ HO + SiF_2$. Silicofluoric acid combines with bases to form salts, if the base be not added in excess; if an excess of base be employed, silica is precipitated, and the whole of the fluorine is separated as a metallic fluoride. In the first case the action may be thus represented: $KO,HO + (HF,SiF_2) = 2\ HO + (KF,SiF_2)$. In the second case: $3\ (KO,HO) + (HF,SiF_2) = 4\ HO + 3\ KF + SiO_2$. Dilute solution of silicofluoric acid produces transparent jelly-like precipitates in the alkaline salts; it is frequently employed as a precipitant of potash. With salts of baryta the acid gives a white crystalline precipitate.

§ II. BORON (B=10·9).

Calcd. Sp. Gr. of Vapour (*Comb. Vol*=2), 0·753.

(391) BORON is the combustible radicle of the acid contained in borax, whence it derives its name. In nature it is always met with in combination with oxygen. It is a body which occurs in comparatively sparing quantities, and only in a few localities. In its properties, and its mode of combination, it presents considerable

analogy with silicon, and, like it, may be obtained in three distinct modifications, the crystalline (B_α), the graphitoid (B_β), and the amorphous form (B_γ).

Amorphous Boron, B_γ.—Berzelius obtained boron by a process analogous to that employed in the case of silicon. The borofluoride of potassium, a sparingly soluble salt, is made by saturating hydrofluoric with boracic acid, neutralizing the liquid with carbonate of potash, and washing the compound with cold water; it is then dried at a heat a little below redness. When cold it is mixed with an equal weight of potassium, and heated in a covered iron crucible. The fluoride of potassium is removed by hot water. $KF,BF_3 + 3K = 4KF + B$.

Boron as thus obtained is an amorphous dull olive-green powder, which, before it has been strongly ignited, soils the fingers, and is dissolved by pure water in small quantity, forming a greenish yellow solution; from which, however, it is precipitated unchanged on adding a little solution of sal ammoniac. Boron is not oxidized by exposure to air, to water, or to solutions of the alkalies, whether cold or boiling. It is, however, easily oxidized when treated with nitric acid or with aqua regia. After exposure to intense heat in vessels from which air is excluded, it becomes denser, and darker in colour. It may be fused by the application of a heat still more intense than that required to melt silicon. As first obtained, boron exhibits a strong affinity for oxygen, and, if heated in air or in oxygen, takes fire below redness, burning with a red light and emitting vivid scintillations; it is thus converted superficially into boracic acid, which melts and protects a portion of the boron. If mixed with nitre and heated to redness, it deflagrates powerfully. It is also oxidized when ignited with hydrate of potash; and when heated with carbonate of potash in fusion it decomposes the carbonic acid, setting charcoal free, and forming borate of potash. Pulverulent boron, like silicon, is a non-conductor of electricity.

Boron may be obtained in the amorphous form in large quantity by the following method (Wöhler and Deville; *Liebig's Annal.* cv. 67):—1500 grains of fused anhydrous boracic acid is coarsely powdered and mixed rapidly with 900 grains of sodium cut into small pieces. The mixture is then introduced into a cast-iron crucible previously heated to bright redness; 700 or 800 grains of solid but previously fused chloride of sodium are placed upon the top of the mixture, and the crucible is covered. As soon as the reaction is over, the still liquid mass is thoroughly stirred with an iron rod, and poured, whilst red hot, in a slender stream into a large and deep vessel containing water acidulated with

hydrochloric acid. The pulverulent boron is then collected on a filter and washed with acidulated water till the boracic acid is got rid of; after which the washing may be continued with pure water, until the boron begins to run through the filter. It must finally be dried upon a porous slab without the application of heat.

Crystallized Boron, B_α.—In order to convert the amorphous into the crystallized form, the following method may be adopted:—A small Hessian crucible is lined with the pulverulent boron made into a paste with water, and the boron is pressed in strongly, as in the ordinary mode of lining a crucible with charcoal. In the central cavity a piece of aluminum weighing from 60 to 90 grains is placed; the cover is luted on and the crucible enclosed in a second, the interval between the two being filled with recently ignited powdered charcoal. The outer crucible is next closed with a luted cover, and the whole exposed for a couple of hours to a heat sufficient to fuse nickel. The temperature is then allowed to fall; and when cold the contents of the inner crucible are digested in diluted hydrochloric acid, which dissolves out the aluminum; beautiful crystals of boron are left, generally transparent, but of a dark brown colour. A quantity of *graphitoid* scales of boron (B_β) are formed at the same time, in pale, copper-coloured, opaque six-sided plates.

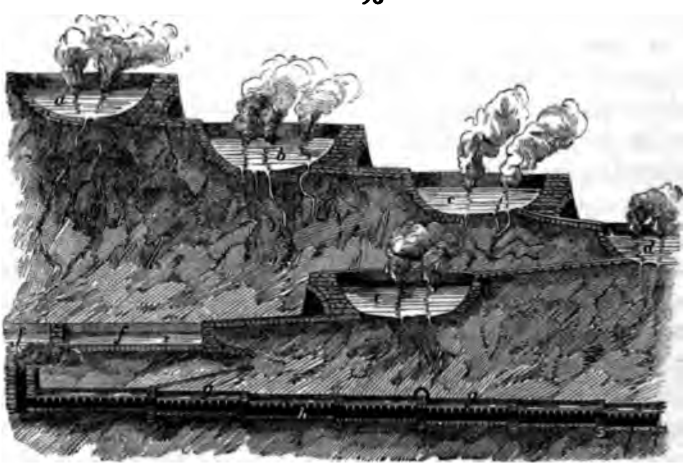
Crystallized boron has a sp. gr. of 2·68; it assumes the form of transparent octohedra belonging to the pyramidal system. These crystals when pure are nearly colourless, but they usually contain traces of foreign matters which give them a pale yellow or red colour; they refract light powerfully, and are hard enough to scratch the ruby, and even sensibly to wear away the diamond. Crystallized boron burns imperfectly in oxygen when heated to full whiteness, and becomes coated with a layer of fused boracic acid. It however burns easily when heated to redness in dry gaseous chlorine, becoming converted into the gaseous terchloride of boron. No acid or mixture of acids has any action upon either crystalline or graphitoid boron.

Boron, like titanium, enters into direct combination with nitrogen at a high temperature; a quantity of this nitride is formed as a grey coherent mass during the preparation of crystallized boron. Pulverulent boron, when heated in a current of dry ammoniacal gas, becomes incandescent, and is converted into nitride, whilst hydrogen is liberated. Boron in all its forms burns freely in chlorine: when ignited in contact with steam, with sulphuretted hydrogen, and with hydrochloric acid, it decomposes them, but the latter is attacked with some difficulty; boracic acid,

sulphide of boron, and chloride of boron being formed respectively, whilst hydrogen is liberated.

(392) Boracic Acid ($BO_3=35$): *Crystallized* (BO_3, 3 HO).—This acid, which is considered as a teroxide of boron, is the only known compound of oxygen and boron. It is found combined with soda as a biborate in the *tincal* obtained from Thibet, and in a crystallized borate of lime and magnesia from the western coast of South America; but it is also met with in the uncombined state in some volcanic districts, where, accompanied by sulphuretted hydrogen, it issues in small quantity along with the jets of steam or *fumerolles*, maintained by the action of subterranean fire. These, at Monte Cerboli and Monte Rotondo, in Tuscany, are directed into small lagoons or artificial basins, such as those shown in fig. 293, the waters of which on evaporation yield a crude boracic

Fig. 293.



acid, from which a large proportion of the borax of commerce is now manufactured. According to the ingenious suggestion of Lardarello, the heat supplied by the fumerolles themselves is employed in this evaporation. Water from the adjacent springs is directed into the uppermost basin, *a*; here it stays for twenty-four hours, and is run off after successive intervals of twenty-four hours into each of the four lower basins, *b*, *c*, *d*, *e*. From the last of these it flows into settling vats, *f*, *f*, where in the course of twenty-four hours more, the suspended matters subside. The supernatant liquid, which contains from 1½ to 2 per cent. of boracic acid, is then decanted into shallow leaden evaporating pans, *g*, *g*, heated by the vapours of several fumerolles, which circulate underneath in flues, *h*, arranged for the purpose. In twenty-four hours the

liquor is reduced to about half its bulk; it is then transferred to a smaller pan, on a lower level, where it is allowed to evaporate for twenty-four hours longer: it is again transferred to a smaller pan, when after the lapse of twenty-four hours more it has acquired a density of 1·07 or 1·08, and is sufficiently concentrated to crystallize on cooling. Sulphate of lime in abundance is deposited in the pans during these evaporations, and it requires removal from time to time. About two thousand tons of the crude acid are now (1860) annually thus procured in Tuscany. The crude acid, however, seldom contains more than three quarters of its weight of the pure crystallized acid, the remainder consisting principally of sulphate of ammonia with small quantities of sulphate of alumina, and of other alkaline and earthy sulphates, a peculiar organic matter, and a small proportion of silica.

The commercial acid is purified by adding to it carbonate of soda to saturation, and thus forming borax, which is obtained nearly pure by crystallization (494).

In order to procure the acid, purified borax is dissolved in 4 parts of boiling water, and to the hot solution, oil of vitriol equal in weight to that of one fourth of the borax employed, diluted with a little water, is added. In this process sulphate of soda is formed, and boracic acid is liberated. The sparingly soluble boracic acid crystallizes out on cooling, in pearly looking scales which feel greasy to the touch; they contain 3 atoms of water to 1 of acid. It is not however quite pure, as it always retains a little sulphuric acid. To remove this, the crystals are washed with ice-cold water, dried, and fused in a platinum crucible, and on redissolving the mass in 4 times its weight of boiling water, the acid crystallizes, on cooling, in a state of purity.

The composition of this acid is the following:—

	Anhydrous.			Crystallized.		
Boron	B =	10·9	or 31·23	B =	10·9 or	56·39
Oxygen	O_3 =	24·0	68·77	O_3 =	24·0	
Water				$3HO$ =	27·0	43·61
Boracic acid	BO_3 =	34·9	100·00	$BO_3, 3HO$ =	61·9	100·00

Properties.—The crystals of boracic acid effloresce and lose two thirds of their water at a gentle heat, and at a slight increase of temperature become anhydrous; at a red heat, or a little below, the anhydride fuses to a transparent, viscid, ductile glass, which remains clear as it cools. It gradually absorbs moisture from the air, and crumbles to pieces. Boracic acid communicates to its compounds the property of ready fusibility; indeed it is chiefly on this account that it is valued. Many of the borates are admirably

adapted for fluxes, which are applied in glazes for porcelain, and in the melting of gold and silver.

Boracic acid is sparingly soluble in cold water, but it is dissolved by 3 times its weight of boiling water; the solution has a bitterish and scarcely sour taste; if allowed to evaporate upon turmeric paper, it turns the paper brown, as an alkali would do; it gives to litmus a purplish red-tint, instead of the usual bright red of the stronger acids. It gradually decomposes solutions of the carbonates even in the cold; but, on the other hand, a brisk current of carbonic acid or of sulphuretted hydrogen will cause a separation of boracic acid in crystals from a strong solution of borax. Boracic acid is soluble in alcohol, and the solution burns with a characteristic green flame. It is not possible to evaporate a solution of boracic acid either in alcohol or in water without losing a portion of the acid, for the vapour always carries with it an appreciable amount of the acid; if steam at a high temperature be transmitted over boracic acid, the acid is volatilized in considerable quantities.

Borates.—Boracic anhydride is but very slowly volatilized by ignition, and hence, though its affinities are exceedingly feeble, it at high temperatures expels all acids more volatile than itself, when fused with their salts. It enters into combination with the alkaline bases in a great variety of proportions, resembling silicic acid in this respect, as in some others. Although many of these salts contain more than 1 atom of acid, they all restore the colour of reddened litmus paper. A sexborate of potash ($KO, 6\ BO_3 + 10\ Aq$) may be obtained in crystals, and a terborate ($KO, 3\ BO_3 + 8\ Aq$) has also been crystallized. The borates of the alkalies are freely soluble, those of the other bases are only imperfectly soluble; none of the borates, however, are so insoluble as to furnish an accurate mode of ascertaining the quantity of boracic acid present in solution by the formation of a precipitate. All the sparingly soluble borates are dissolved by diluted nitric acid. In analysing a borate it is usual to determine the amount of all the other acids and bases, and other constituents, and to estimate the deficiency as boracic acid. It is not unlikely that boracic acid may have been overlooked in several minerals, as its detection in small quantities is rather difficult.

(393) A *sulphide*, a *chloride*, and a *bromide* of boron may be prepared by methods similar to those employed to obtain the corresponding compounds of silicon. The *chloride of boron* ($BCl_3 = 117{\cdot}4$; *Sp. gr.* 4·079; *Comb. vol.* 4) is gaseous at ordinary temperatures; it fumes strongly in air, and is instantly decomposed

by water into hydrochloric and boracic acids. It has the following composition:—

			By weight.		By volume.			Sp. gr.
Boron	B	=	10·9 or	9·29	2 or	0·5	=	0·376
Chlorine	Cl_3	=	106·5	90·71	6	1·5	=	3·679
Chloride of boron	BCl_3	=	117·4	100·00	4	1	=	4·055

Four volumes of this chloride unite with 6 volumes of ammonia, and become condensed to a volatile crystalline saline body.

(394) FLUORIDE OF BORON (BF_3=67·9); *Sp. Gr.* 2·312; *Comb. Vol.* 4.—Boron forms with fluorine a compound analogous to the fluoride of silicon. It is best prepared as follows: 2 parts of fluor-spar and 1 of vitrified boracic acid, both in fine powder, are intimately mixed, and intensely ignited in a wrought-iron tube closed at one end: decomposition occurs thus: $3\ CaF + 4\ BO_3 = 3\ (CaO,\ BO_3) + BF_3$. Borate of lime remains in the tube, and the fluoride of boron passes over as a colourless gas, which may be collected over mercury. The composition of the fluoride of boron is the following:—

			By weight.		By vol.			Sp. gr.
Boron	B	=	10·9 or	16·07	2 or	0·5	=	0·376
Fluorine	F_3	=	57·0	83·93	6	1·5	=	1·969
Fluoride of boron	BF_3	=	67·9	100·00	4	1·0		2·345

Fluoride of boron does not support combustion; it has an irritating odour, and fumes densely in the air. It is instantly absorbed by water, which dissolves 700 times its volume of the gas, with rapid rise of temperature, whilst it increases in density to 1·77, and forms an oily-looking, fuming, and corrosive acid liquid, which chars organic matter as powerfully as oil of vitriol. This solution has been called *borofluoric acid.* The reaction which occurs when the gas comes into contact with water is sufficiently simple, $BF_3 + 3\ H\dot{O}$, yielding (BO_3, 3 HF). When heated, a part of the gas escapes, and the specific gravity of the liquid becomes reduced to 1·584; when of this density it distils unchanged, and contains two equivalents of water, the formula of the aqueous solution becoming BO_3, 3 HF + 2 HO. Borofluoric acid is also easily prepared by saturating hydrofluoric acid with boracic acid, keeping the mixture cool, and then concentrating it in platinum vessels till dense fumes arise.

When largely diluted with water, one fourth of the boron is separated in the form of boracic acid, and another compound is found in solution, termed *hydrofluoboric acid.* In composition this body

somewhat resembles the silicofluoric acid, though it is not strictly analogous to it. Its formation is readily explained by the following equation, from which it will be seen that hydrofluoboric acid contains the elements of 1 atom of hydrofluoric acid and 1 atom of fluoride of boron:—

$$4\,BF_3+3\,HO=BO_3+3\,(HF,BF_3).$$

So strong is the tendency to the formation of this compound in dilute solutions, that if boracic acid be added to a solution of fluoride of potassium or of ammonium, for each equivalent of boracic acid present, 3 equivalents of potash or of ammonia are liberated; and fluoboride of the base is formed: for example, $4\,KF+BO_3, 3\,HO=(KF,BF_3)+3\,(KO,HO)$.

(395) *Nitride of Boron* (BN).—As already mentioned, boron combines with nitrogen at a red heat with great avidity. Nitride of boron may also be obtained by transmitting a current of dry nitrogen gas over a mixture of 1 part of pure, finely-powdered charcoal, with 4 parts of fused boracic acid, exposed to a full white heat in a porcelain tube. It may likewise be procured readily by mixing 1 part of anhydrous borax with two parts of sal ammoniac, and heating it to a full redness in a covered platinum crucible; a white, infusible, porous mass is left, which, when boiled with diluted hydrochloric acid and well washed, yields the nitride of boron as a white, light, amorphous, insoluble powder, which feels like talc when rubbed upon the skin. It may be heated in hydrogen or in chlorine without change; it is but very slowly acted upon by concentrated acid or alkaline solutions; but when fused with hydrate of potash it is resolved into ammonia and boracic acid, which latter combines with the potash. In a current of steam it is completely converted into borate of ammonia; $BN+4\,HO$ yielding H_4NO, BO_3. It is also decomposed when heated with easily reducible metallic oxides, such as those of lead or copper; deutoxide of nitrogen being evolved.

CHAPTER IX.

OTHER COMPOUNDS OF THE NON-METALLIC ELEMENTS.

§ I. Compounds of Hydrogen and Oxygen.

(396) Binoxide or Deutoxide of Hydrogen (*Oxygenated Water*) ($HO_2=17$): *Sp. Gr. of Liquid*, 1·453.—Water is not the only compound of oxygen with hydrogen. Thénard, in the year 1818,

discovered a remarkable substance, which, as it contains 2 equivalents of oxygen in combination with 1 equivalent of hydrogen, is termed *binoxide of hydrogen*. It is a colourless liquid, of syrupy consistence, with an odour somewhat resembling that of chlorine very much diluted; it remains liquid at a temperature of — 22°. This binoxide is a very unstable compound; a temperature of about 70° F. is sufficient to cause the oxygen to begin to escape in small bubbles, and when heated to the boiling-point of water, the gas is evolved with a rapidity almost amounting to an explosion. The liquid is soluble in water in all proportions; when diluted it is less easily destroyed by elevation of temperature, though ebullition for a few minutes is sufficient to expel the whole of the additional equivalent of oxygen, water alone remaining. This circumstance furnishes an easy method of analysing the binoxide of hydrogen. A given weight of the liquid is placed in a small retort, and diluted with 10 or 12 times its bulk of water; the temperature is raised to ebullition, oxygen is given off freely, and the gas is collected over mercury and measured when cool: the weight of the oxygen can be calculated from its bulk, and deducting the weight thus obtained from that of binoxide operated upon, it will be found that for each 8 grains of oxygen expelled, 9 of water remain; consequently, as water contains 1 grain of hydrogen combined with 8 grains of oxygen, the binoxide of hydrogen will contain 1 grain of hydrogen united with 16 grains of oxygen.

Binoxide of hydrogen bleaches a solution of litmus, and many vegetable colours; a drop of it, if placed upon the tongue, blanches it, and destroys sensation for a time; the taste of the liquid is astringent and somewhat metallic. By means of binoxide of hydrogen the black sulphide of lead (PbS) is converted into sulphate of the metallic oxide (PbO,SO_3), and many metallic protoxides become oxidized to the maximum.

The binoxide of hydrogen, however, is not only decomposed by substances which possess an affinity for oxygen, but the mere contact of many finely divided metals and metallic oxides which do not undergo any permanent change, occasions its decomposition; gold, silver, and platinum produce an instantaneous evolution of oxygen gas, which is the more rapid the finer the subdivision of the body by which the decomposition is occasioned. A similar effect is produced by contact with the oxides of these metals, or with the peroxide of manganese or of lead. It is especially to be remarked that the oxides of silver, of gold, and of platinum, not only decompose the binoxide, but they are themselves reduced to the metallic state. These decompositions are all rendered less

rapid by the addition of a few drops of sulphuric or hydrochloric acid, but are hastened by the addition of a little free alkali. If the binoxide of hydrogen in its concentrated form be allowed to fall drop by drop upon oxide of silver, peroxide of manganese, or upon metallic silver, platinum, or osmium in a finely divided state, it is decomposed with explosion and great elevation of temperature.

(397) *Preparation.*—Owing to the unstable character of the binoxide of hydrogen, its preparation is attended with great difficulty, although in principle the process is simple. An indirect method is resorted to for procuring it: caustic baryta (BaO), when heated to dull redness in a current of oxygen gas, combines with an additional equivalent of oxygen, and becomes peroxide of barium (BaO_2): when this substance is moistened with water it forms a hydrate (BaO_2, 6 HO). The binoxide of hydrogen is obtained from this hydrated compound by decomposing it by means of hydrochloric acid. The hydrated peroxide of barium is reduced to a paste by grinding it in a mortar with water, and is added in small quantities at a time to hydrochloric acid diluted with water, and kept cool by immersing the vessel in ice and water; the peroxide is gradually dissolved without effervescence, chloride of barium and binoxide of hydrogen being formed; $BaO_2,HO+HCl$ yielding $HO_2+HO+BaCl$. When the hydrochloric acid is nearly saturated with the peroxide, the chloride of barium is decomposed by the cautious addition of diluted sulphuric acid; an insoluble sulphate of baryta is precipitated, whilst hydrochloric acid is set free, and is able to decompose a fresh quantity of peroxide of barium, which must be added with the same precautions as at first. The addition of sulphuric acid produces no change on the binoxide of hydrogen which is present in the solution: it is merely an expedient for getting rid of the baryta and liberating the hydrochloric acid.*

The sulphate of baryta is next removed by filtration, and the liquid thus left is simply a very dilute solution of binoxide of hydrogen with an excess of hydrochloric acid. This acid is again able to decompose a fresh portion of the peroxide of barium. The same series of operations is repeated upon the liquid three or four times in succession, alternately adding peroxide of barium, and removing the barium in the form of sulphate of baryta; until a liquid is obtained which consists of dilute binoxide of hydrogen

* Pelouze substitutes silicofluoric for hydrochloric acid in decomposing the peroxide of barium; it shortens the operation, by removing the baryta at once in the form of an insoluble silicofluoride of barium.

containing 30 or 40 times its bulk of oxygen, and a large quantity of hydrochloric acid. The hydrochloric acid has now to be removed, and this is effected by adding sulphate of silver, until a trace only of hydrochloric acid is left in the liquid. Sulphuric acid is thus substituted for the hydrochloric acid, which is precipitated in the form of the insoluble chloride of silver, while the binoxide of hydrogen remains unchanged in the liquid.

The sulphuric acid is now got rid of by the careful addition of baryta water, which is at last added drop by drop, so as to remove the whole of the sulphuric acid without introducing any excess of baryta: the liquid is once more filtered, and is now a pure solution of the binoxide of hydrogen in water; finally, it may be transferred to a basin and placed over sulphuric acid in the exhausted receiver of the air-pump. The water evaporates much more rapidly than the binoxide of hydrogen, which is thus at length obtained in a concentrated form.

Schönbein has shown (*Ann. de Chimie,* III. lviii. 479) that in various processes where ozone is formed, small quantities of binoxide of hydrogen are also produced; and in the electrolysis of acidulated and saline solutions when ozone is formed, traces of binoxide of hydrogen are likewise produced if the operation is conducted at a low temperature, the proportion of gaseous oxygen collected in the voltameter being then always a little below the theoretical quantity.

§ II. Compounds of Carbon and Hydrogen.

(398) The compounds of carbon with hydrogen are numerous. They are all derived from the decomposition of bodies of organic origin. Many of these bodies exhibit absolute identity in the proportion of the two elements which compose them, although they are endowed with properties perfectly distinct; and, from the different densities of these bodies in the gaseous or vaporous condition, it is obvious that the condensation of their particles is different. For example, the following are a few of the many compounds which contain in 100 parts 85·71 of carbon and 14·29 of hydrogen:—

Olefiant gas .	C_4H_4 .	specific gravity,		0·978
Oil gas . . .	C_8H_8 .	„	„	1·852
Naphthene. .	$C_{16}H_{16}$.	„	„	3·900
Cetylene . .	$C_{32}H_{32}$.	„	„	8·007

Such bodies are said to be *polymeric.* At present it will not be

necessary to describe more than three compounds of carbon and hydrogen—viz., olefiant gas, marsh gas, and oil gas.

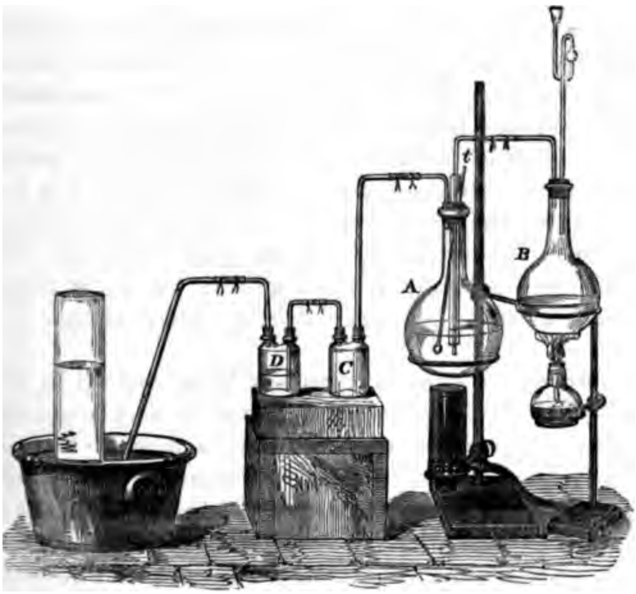
(399) OLEFIANT GAS; *Elayl*, or *Ethylene* ($C_4H_4=28$); *Sp. Gr.* 0·9784; *Comb. Vol.* 4.

Preparation.—1.—If 2 measures of concentrated sulphuric acid be mixed with 1 measure of alcohol, in a retort capable of containing at least four times the bulk of the liquid introduced, on distillation a transparent colourless gas is obtained, consisting of carbon and hydrogen. It is accompanied by the vapour of ether, and towards the close of the process by sulphurous acid in large quantity. The olefiant gas, as this compound of carbon and hydrogen is termed, at first comes off freely, but by degrees the mixture blackens and becomes thick, and froths up considerably, so that the operation requires careful watching in its latter stages: this tendency to frothing may be much diminished by adding to the mixture, before applying heat, a quantity of sand equal in weight to half that of the acid employed. The gas may be purified by causing it first to pass through an empty bottle, kept cool by immersion in water, in order to condense the vapours of alcohol and ether; then washing it in a solution of potash, to absorb sulphurous acid, removing the last traces of ether by allowing it to bubble up through concentrated sulphuric acid, and finally drying it, when necessary, by causing it to traverse a tube filled with fragments of pumice moistened with oil of vitriol.

2.—A more elegant method of obtaining the gas was devised by Mitscherlich: it is shown at fig. 294, in which A represents a flask containing oil of vitriol, diluted with one-third of its weight of water; B is a second flask, containing alcohol; C an empty bottle for condensing any alcohol and water which may distil over; D is a wash-bottle containing a solution of potash. The acid in A is raised to the temperature of 325°, at which point it is maintained, by watching the thermometer *t*, and raising or lowering the flame accordingly; the alcohol in B is then slowly converted into vapour, and made to pass over into the flask, A, in such quantity as just to maintain the boiling point of the acid at from 325° to 330°; at this particular temperature, the alcohol, by contact with sulphuric acid, is completely decomposed into olefiant gas and water. Sulphuric acid possesses the remarkable property of producing this decomposition without itself apparently undergoing any change, with the exception of becoming slightly brown; the bulk of the sulphuric acid does not alter during the operation, and the same limited amount of sulphuric acid may be employed to convert an in-

definite and almost unlimited amount of alcohol into olefiant gas and water.

FIG. 294.



This remarkable decomposition may be thus explained : alcohol enters into combination with sulphuric acid, and forms a peculiar compound acid, the sulphovinic or sulphethylic acid, which is decomposed by a high temperature : the sulphuric acid is liberated in an unchanged condition, whilst the alcohol breaks up into water and olefiant gas, at the same time a portion of the water with which the acid was at first diluted distils off, and accompanies the olefiant gas :—

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} + 2\,(\overbrace{HO,SO_3}^{\text{Sulph. acid.}}) \text{ becomes } \overbrace{HO,C_4H_5O,S_2O_6}^{\text{Sulphethylic acid.}} + 2\,\overbrace{HO}^{\text{Water.}};$$

and by heat

$$\overbrace{HO,C_4H_5O,S_2O_6}^{\text{Sulphethylic acid.}} \text{ becomes } \overbrace{2\,(HO,SO_3)}^{\text{Sulphuric acid.}} + \overbrace{C_4H_4}^{\text{Olefiant gas.}}.$$

3.—Olefiant gas is also obtained, mixed with various other gaseous compounds, during the destructive distillation of a large number of bodies of organic origin,—particularly the resins, the fats and oils, and the different varieties of pit-coal. It forms an important component of coal gas.

Properties.—Olefiant gas is transparent and colourless ; it has

a faint, sweetish, alliaceous odour, and is soluble in about 12 times its bulk of cold water. It was liquefied by Faraday under great pressure, but remained unfrozen at -166°. Olefiant gas does not support life or combustion, but is itself very inflammable, and burns with a white luminous flame, depositing carbon abundantly upon cold bodies which are introduced into its flame. If a succession of electric sparks be passed through the gas, or if it be transmitted through porcelain tubes heated to bright redness, it is decomposed: half its carbon is deposited, and another compound of carbon with hydrogen (light carburetted hydrogen) is formed, which occupies the same volume as that of the olefiant gas from which it was produced. If the heat to which the gas is subjected be extremely intense, all the carbon is deposited, and for each volume of gas decomposed 2 volumes of hydrogen are liberated.

The composition of olefiant gas may be ascertained by detonation with oxygen; the explosion, however, is very powerful, and requires care, otherwise the eudiometer will be broken. One volume of the gas requires for its complete combustion 3 volumes of oxygen; 2 volumes of carbonic acid remain and represent 2 out of the 3 volumes of oxygen, whilst the other volume of oxygen becomes condensed as steam, and consequently combines with 2 volumes of hydrogen; 2 volumes of hydrogen and 2 of carbon vapour are therefore condensed in olefiant gas into the space of 1 volume. From these data the composition of the gas may be represented in the following manner:—

		By weight.		By vol.	Sp. gr.
Carbon	C_4 =	24	or 85·71	8 = 2·0	= 0·829
Hydrogen	H_4 =	4	14·29	8 = 2·0	= 0·138
Olefiant gas	C_4H_4 =	28	100·00	4 = 1·0	= 0·967

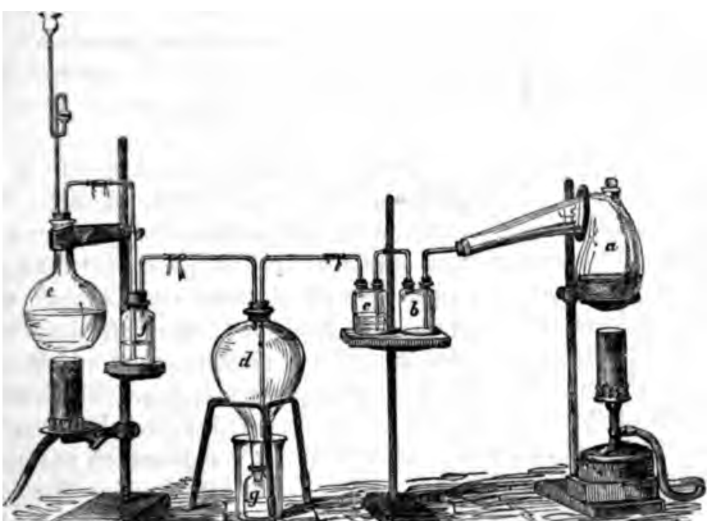
Olefiant gas is slightly soluble in alcohol, in oil of turpentine, and in the fixed oils. It combines with sulphuric anhydride, forming with it a peculiar compound; hence it is completely absorbed by fuming sulphuric acid, and it is somewhat soluble in ordinary oil of vitriol; the latter by brisk agitation with the gas may be made to take up 30 or 40 times its volume, forming sulphethylic acid (981). It also combines with, and is absorbed by, the perchloride of antimony. Olefiant gas, when mixed over water with an equal volume of chlorine, unites with it and becomes condensed to a heavy, sweetish, aromatic liquid: it collects into oily-looking drops, which sink in water: it was owing to this reaction that the name of olefiant (or oil-producing) gas was given to it,

and the oily body itself is commonly known as *Dutch liquid*, from the circumstance of its discovery in Holland. If 1 measure of olefiant gas be mixed with 2 measures of chlorine, the mixture may be kindled by a lighted taper, and will burn quietly, depositing the whole of the carbon of the gas in the form of a dense smoke, whilst the hydrogen unites with the chlorine to form hydrochloric acid.

(400) DUTCH LIQUID, or *Bichloride of Ethylene* (C_4H_3Cl,HCl) or ($C_4H_4Cl_2$), = 99; *Sp. Gr. of Liquid*, 1·28 at 32°; *of Vapour*, 3·45; *Boiling Pt.* 184°; *Comb. Vol.* 4.—This is a compound of considerable interest, as it is the substance from which the chlorides of carbon were originally obtained by Faraday; and the careful study (since made by Regnault) of the stages of the process by which these substances are formed, illustrates in a striking manner the mode in which compounds may be procured by a process of substitution in which the hydrogen of the original body is displaced by chlorine.

Preparation.—1.—Dutch liquid is required in considerable quantity for these experiments; it may be obtained by means of an apparatus similar to that represented in fig. 295: *a* is a retort

FIG. 295.



containing the mixture of sulphuric acid and alcohol, which is to furnish the olefiant gas; *b* is an empty bottle to condense the

vapours of alcohol and ether; *c* a vessel containing sulphuric acid for absorbing any uncondensed vapour of ether; *d* is a large glass receiver, in which the current of olefiant gas is mingled with a stream of chlorine disengaged from the flask, *e*, and which is washed by passing through the water contained in the bottle, *f*. The olefiant gas is supplied so that it shall always be in slight excess over the chlorine; and both gases must be moist, in order to favour the reaction; the operation is best conducted in full diffused daylight. The two gases combine rapidly, and condense in oily drops, which run down the sides of the receiver, *d*, and are collected in the bottle, *g*.

Limpricht has simplified this apparatus by transmitting the olefiant gas through the mixture of oxide of manganese and hydrochloric acid, from which the chlorine is generated. The olefiant gas is conveyed into this mixture by means of a bent tube which passes through the tubulure of the retort, and the Dutch liquid, as it is formed, distils over into a receiver connected with the retort.

2.—Another method by which Dutch liquid may be prepared consists in transmitting olefiant gas through perchloride of antimony so long as it is absorbed. The product is submitted to distillation, and the heat is maintained so long as the distillate yields an oily liquid on the addition of water.

The oil which is obtained by either of these processes is decanted, agitated with successive portions of oil of vitriol so long as they become blackened, and the product purified by redistillation.

Dutch liquid is a colourless aromatic liquid which is not soluble in water, but freely soluble in ether and in alcohol. The simplest supposition respecting the composition of this body, since its vapour consists of equal volumes of chlorine and of olefiant gas, is that 2 volumes or 1 equivalent of chlorine are combined with 2 volumes of olefiant gas, and condensed into half their bulk (C_2H_2Cl), whence the atomic weight of olefiant gas should be one-half of that which has been given in paragraph 399. The investigations of Regnault have, however, rendered it probable that the composition of Dutch liquid is not correctly represented so simply, that its atomic formula is not C_2H_2Cl, but just double. The usual combining volume of an atom of such vapours is 4 times that of the atom of oxygen, and the density of the vapour, as obtained by experiment, coincides almost exactly with that required by the supposition that the formula is ($C_4H_4Cl_2$):—

			By weight.		By volume.			Sp. gr.
Chlorine	Cl_2	=	71 or	71·68	4 or	1	=	2·453
Carbon	C_4	=	24	24·28	8	2	=	0·829
Hydrogen	H_4	=	4	4·04	8	2	=	0·138
Dutch liquid	$C_4H_4Cl_2$	=	99	100·00	4	1	=	3·420

The formula for Dutch liquid is commonly written C_4H_3Cl,HCl.

It was ascertained by Faraday that when Dutch liquid is exposed in a glass vessel with chlorine to the direct rays of the sun, taking care to renew the chlorine as long as it is absorbed, the liquid is ultimately converted into the white crystalline and volatile sesquichloride of carbon, whilst a very copious disengagement of hydrochloric acid gas takes place.

Regnault has shown that this formation of the sesquichloride of carbon is the result of the interchange of chlorine for hydrogen in the composition of the Dutch liquid; so that sesquichloride of carbon may be regarded as Dutch liquid in which the place of the hydrogen is supplied by chlorine: and he has described a series of compounds intermediate between this liquid and Faraday's sesquichloride of carbon. For example:—if chlorine be transmitted through Dutch liquid, the gas is rapidly absorbed, and the liquid acquires a yellow colour, which disappears with copious evolution of hydrochloric acid when it is brought into the sun's rays: by carefully adjusting the addition of chlorine, a new liquid is obtained, which boils at 239°, and has a specific gravity of 1·422. Two atoms of chlorine act upon 1 atom of Dutch liquid, 1 atom of the chlorine combining with 1 of hydrogen to form the disengaged hydrochloric acid, while the second atom of chlorine takes the position of the displaced hydrogen: thus, $(C_4H_3Cl,HCl) + 2\ Cl$ furnish $(C_4H_2Cl_2,HCl) + HCl$. This new liquid may be made to absorb a fresh quantity of chlorine, and in the sun's rays it undergoes a change analogous to the preceding one; a liquid is formed which boils at 275°, and has a density of 1·576; $(C_4H_2Cl_2,HCl) + 2\ Cl$ yielding $(C_4HCl_3,HCl) + HCl$. This third liquid, if again acted upon by two additional atoms of chlorine, undergoes a further similar decomposition; a still heavier liquid, of specific gravity 1·663, boiling at 307°, is produced, $(C_4HCl_3,HCl) + 2\ Cl$ becoming $(C_4Cl_4,HCl) + HCl$: and finally, this fourth liquid, when acted upon by an excess of chlorine, loses the remaining atom of hydrogen, and becomes the solid sesquichloride of carbon; for $(C_4Cl_4,HCl) + 2\ Cl = (C_4Cl_4,Cl_2) + HCl$; the successive products having the composition and density indicated in the following table:—

Chlorinated Compounds derived from Dutch Liquid.

Name of Compound.	Boiling point °F.	Specific gravity.		Formula.
		Liquid.	Vapour.	
Dutch liquid	184	1·280	3·45	C_4H_3Cl,HCl
Chlorinated ditto . .	239	1·422	4·613	$C_4H_2Cl_2,HCl$
Bichlorinated ditto . .	275	1·576	5·769	C_4HCl_3,HCl
Terchlorinated ditto .	307	1·663	7·08	C_4Cl_4,HCl
Sesquichloride of carbon	356		8·157	C_4Cl_4,Cl_2

It will be seen that as the quantity of chlorine increases, the boiling point rises, and the density both of the liquid and of the vapour increases: in every case 1 atom of the compound yields 4 volumes of vapour (see also § 919 and 1021).

(400 *a*) *Bibromide of Ethylene* ($C_4H_4Br_2$=188), *Sp. Gr. of Liquid,* 2·163; *of Vapour,* 6·485; *Boiling Pt.* 265°.—Cahours has obtained a series of compounds from olefiant gas containing bromine: the bibromide of ethylene or brominated compound corresponding to Dutch liquid, may be procured by placing bromine in a flask and transmitting into it a current of olefiant gas as fast as it is absorbed, a rapid combination occurs, the temperature rising sensibly. The bromine is gradually decolorized, and an ethereal liquid of aromatic odour, and a pungent but sweet taste, is obtained. It may be purified by agitating it with caustic potash, then distilling from oil of vitriol and subsequently from caustic baryta.

Biniodide of Ethylene ($C_4H_4I_2$=282), or the compound of olefiant gas with iodine, corresponding to Dutch liquid, is a solid which crystallizes in long, colourless, silky needles, or in flexible plates: it has a sweetish taste and an ethereal penetrating odour, which causes headache; it melts at 163°, and forms a crystalline mass on cooling. It may be sublimed in a current of olefiant gas, but cannot be sublimed in air or *in vacuo* without being decomposed; it slowly undergoes spontaneous decomposition, becoming brown at ordinary temperatures, especially under the influence of light. This compound may be obtained by placing iodine in a flask with a long neck, heating it by means of a water-bath to 130° or 140°, and transmitting a current of olefiant gas. The iodine melts and absorbs the gas, whilst the new compound as it is formed undergoes partial sublimation. It is also said to be obtained by decomposing iodide of ethyl by transmission through a porcelain tube heated to redness. It may be purified by washing with a weak solution of potash and recrystallization from boiling alcohol.

(401) Light Carburetted Hydrogen: *Subcarburetted Hy-*

drogen; *Marsh Gas*, or *Fire-damp*; *Hydride of Methyl* ($C_2H_4 = 16$); *Sp. Gr.* 0·5596; *Comb. Vol.* 4.

Preparation.—1.—This gas is best obtained in a state of purity by a process recommended by Persoz: $10\frac{2}{3}$ parts of the hydrate of baryta and $10\frac{1}{3}$ of anhydrous acetate of soda, are very intimately mixed, and heated over a charcoal fire in a Florence flask, coated with a luting of fire-clay made into a paste with a solution of borax. The flask is fitted with a cork and bent tube, and the gas is collected over water in the usual way.* A mixture of 2 parts of caustic potash and 3 of quick-lime may be substituted for the hydrate of baryta.

2.—The gas is also easily procured (mingled with nitrogen and carbonic acid), as a result of the decomposition of vegetable matter contained in the mud of stagnant pools; and hence its name of *marsh gas*. In order to collect the gas from this source a bottle may be filled with water, inverted in the pool, and having fastened a funnel into the neck of the bottle, the mud beneath is stirred with a stick; the gas then rises into the bottle in bubbles.

3.—Light carburetted hydrogen is one of the principal constituents of coal gas; it also occurs abundantly in many coal mines, bursting forth unexpectedly from the seams of coal, and blowing out from the fissure for many months together, as though escaping from under high pressure. These natural discharges of the gas the miners term 'blowers.' According to the experiments of Graham, the gas from the Newcastle coal field is free from admixture with olefiant gas, hydrogen, carbonic oxide, and carbonic acid.

Properties.—Subcarburetted hydrogen is a colourless, inodorous, and tasteless gas, scarcely soluble in water, but soluble in alcohol to a small extent: not injurious to life if diluted with air. It does not support combustion, but is itself inflammable, and burns with a yellow luminous flame. By passing through it a continued succession of electric sparks, or by sending it through tubes heated to whiteness, it is decomposed; its carbon is deposited, and a volume of hydrogen, double that of the gas employed, is set at liberty. A mixture of this gas with a variable proportion of olefiant gas constitutes the most important ingredient of coal gas. Chlorine has no effect upon it in the dark, but if the two gases be mixed and exposed in a moist condition to diffused light, hydrochloric and carbonic acids are formed; $C_2H_4 + 8\,Cl + 4HO = 2\,CO_2 + 8\,HCl$. An excess of chlorine converts marsh gas into

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* $$\overbrace{NaO,C_4H_3O_3}^{\text{Acetate of soda.}} + \overbrace{BaO,HO}^{\text{Hydrate of baryta.}} \text{ give } \overbrace{BaO,CO_2}^{\text{Carb. baryta.}} + \overbrace{NaO,CO_2}^{\text{Carb. soda.}} + \overbrace{C_2H_4}^{\text{Marsh gas.}}$$

hydrochloric acid and bichloride of carbon, when the mixture is exposed to light.

Marsh gas requires twice its volume of oxygen for complete combustion. The 3 volumes of the mixed gases after detonation, are condensed into 1 volume; they yield 1 volume of carbonic acid and a little water. Now carbonic acid contains its own bulk of oxygen; it therefore represents one of the 2 volumes of oxygen which have disappeared, whilst the other volume of oxygen has united with 2 volumes of hydrogen and formed water. Light carburetted hydrogen must consequently contain its own volume of carbon vapour and twice its volume of hydrogen, condensed into the space of 1 volume, and its composition may be thus represented:—

			By weight.		By volume.		Sp. gr.
Carbon	C_2	=	12 or	75	4 or	1	= 0·4146
Hydrogen	H_4	=	4	25	8	2	= 0·1382
Marsh gas	C_2H_4	=	16	100	4	1	= 0·5528

When marsh gas is mixed with air, an explosive mixture is formed, which takes fire on the approach of a light, and often occasions accidents attended with loss of life to those who are engaged in coal mines. The fatal results of an explosion of fire-damp in the mine are not, however, limited to the mechanical violence which it occasions to the sufferers. The 'after-damp,' as the miners term it, or vitiated atmosphere that the explosion produces, is often fatal to those employed in other parts of the mine, or to the generous but ignorant and rash survivor who attempts to descend into the pit before it has been properly ventilated, in order to succour his comrades, or to ascertain their fate. From the composition of fire-damp it is obvious that this gas in exploding renders ten times its bulk of atmospheric air unfit for respiration; the 2 volumes of oxygen which 10 volumes of air contain, producing 1 volume of carbonic acid, and 2 volumes of steam which become condensed, leaving 8 volumes of nitrogen at liberty.

It was with a view of discovering some means of preventing these fatal results that Davy instituted those important researches on flame which led him to the invention of the *safety lamp*, an instrument which has prevented many serious accidents, and has enabled many coal-fields to be worked which otherwise must have been abandoned, on account of the abundant escape of fire-damp from the workings.

(402) *Principle of the Safety Lamp.*—The temperature required for the combustion of different bodies varies greatly; some take fire at a very low temperature,—phosphorus, for instance, at the

heat of the body; sulphur at about 480°; others, as olefiant gas and hydrosulphuric acid, need a red heat. A high temperature is however essential to the existence of flames, and particularly of flames produced by the combustion of the hydrocarbons. Subcarburetted hydrogen, although an inflammable gas, requires a much higher temperature to ignite it than most other inflammable bodies; it will not explode when mixed either with less than 4 times its bulk of atmospheric air, or with more than 16 times its volume; the gas in the latter case burns only in immediate contact with the flame of the lamp, for the large volume of air with which it is mixed prevents the temperature from rising to the point necessary for the general conflagration of the gas: the most powerful explosion is occasioned when the gas is mixed with 7 or 8 times its bulk of air.

Combustion may often be carried on below the point of inflammation. The smouldering wick of a taper recently blown out is a case in point. Again, if a glowing coil of platinum wire, or a hot slip of platinum foil, be suspended in a current of coal gas mixed with atmospheric air, the metal will be maintained at a red heat by the rapid combination of the oxygen with the gas, which, however, does not take fire until the platinum becomes heated nearly to whiteness.

Davy found that no explosion could be produced in a mixture of air and fire-damp, through a narrow tube, owing to the cooling influence which the tube exerted upon the gas; and the narrower the tube, the shorter was the length required to produce this protective effect. Hemming's safety tube for the oxyhydrogen blowpipe (294) depends for its efficacy upon the cooling influence which the metallic tubes or channels, formed by the interstices between the wires, exert upon the burning jet of gas: the heat of the flame is in this way prevented from passing backwards and causing the explosion of the mixed gases in the reservoir.

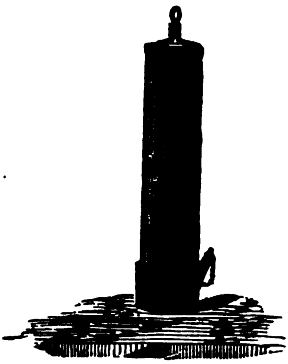
If a stout copper wire be introduced into any flame, a dark space will be observed immediately around the wire, owing to the cooling effect of the metal; a second wire cools the flame still further; and a small flame may be completely extinguished by the reduction of temperature produced by bringing down a coil of wire upon it; but if the same coil be previously heated to redness, and, whilst still hot, be placed over the flame, the latter will continue to burn.

By using wire gauze we may easily cut off the upper part of a flame, the unburned gases being cooled by its means below the point of inflammation: if a piece of gauze with large meshes be employed it will cut off the flame so long as it remains cold, but

the flame will traverse the network as soon as the wire becomes red-hot: with finer meshes (about 400 to the square inch) the conducting power of the metal is sufficient to cool the flame below the point of ignition, even though the wire itself be red-hot. In a similar manner the gas above the gauze may be kindled, and the flame will not pass through to the gas below. Advantage is taken of this circumstance in the laboratory to obtain a smokeless flame by the use of ordinary coal gas:—A metallic chimney, five or six inches long, open below, and furnished at top with a cap of wire gauze is placed over any convenient form of burner; the air enters at the bottom and mixes with the gas; this mixture burns above the wire gauze with a blue flame, which emits scarcely any light, and deposits no smoke upon cold objects, provided that the supply of gas be duly proportioned to that of the air which mixes with it.

These principles were beautifully applied by Davy in the construction of his miner's lamp, which is merely an oil lamp, fig. 296, inclosed within a cylinder of fine wire gauze, provided with a double top, and with a crooked wire, w, which passes up tightly through a tube traversing the body of the lamp, for the purpose of trimming the wick without the necessity for removing the wire covering. When such a lamp is introduced into an explosive atmosphere of fire-damp, the flame is seen gradually to enlarge as the proportion of carburetted hydrogen increases, until at length it fills the entire gauze cylinder; when the gas is in sufficient excess the lamp is entirely extinguished; if it be withdrawn from the explosive mixture while the cylinder appears to be full of flame, the wick is generally rekindled, and the lamp continues to burn in air as usual. Whenever this pale, enlarged flame is seen, the miner must withdraw; for though no explosion can occur while the gauze is sound, yet at that high temperature the metal becomes rapidly oxidized, and might easily break into holes; a single aperture of sufficient size would then determine the fatal explosion.

Fig. 296.



The wire gauze used in the construction of these lamps contains from 700 to 800 meshes in the square inch. In a strong current of air the heated gas may be blown through the apertures of the gauze before its temperature is sufficiently reduced to pre-

vent the explosion, but such an occurrence may be easily guarded against by the use of a screen.

(403) *Nature of Flame.*—It is necessary to the production of flame, that the combustible be of such a nature as to be convertible into vapour before it undergoes combustion, otherwise no flame is produced. Well burned charcoal or diamond burns with a steady glow, unattended with flame, as also does iron wire. None of these substances are susceptible of volatilization at the temperature attending their combustion. Sulphur, phosphorus, and zinc, pass into the aëriform condition before they attain a temperature as high as that produeed by their combination with oxygen, and they, as well as the various combustible gases, burn with flame.

Flame is, in fact, produced whenever a continuous supply of combustible vapour or gas is made to combine at a sufficiently elevated temperature with atmospheric oxygen, or with some gaseous supporter of combustion. In all ordinary cases, therefore, flame is a luminous envelope which forms a limiting surface between the unburned combustible within and the supporter of combustion without.

This hollow structure of flame may be easily shown by experiment. If a wooden match be held for a few seconds across the middle of the flame of a spirit lamp with a large wick, the match will become charred at the edges of the flame, but the intermediate portion will remain uninjured. If a fragment of phosphorus be placed in a small deflagrating spoon, ignited, and then introduced into the middle of the flame, it will be extinguished; but it will burn with its former energy the moment that the spoon is withdrawn from the flame. The tapering form which flames assume, is due to the ascending current produced in the atmosphere by the heat attendant on the combustion. Within the burning portion of the flame is an atmosphere of unburned combustible matter: by inserting into a flame, such as that of a wax candle, just above the wick, the lower extremity of a glass tube, open at both ends, about one-third of an inch in diameter, and five or six inches long, the gases in the interior may be drawn off, and may be ignited at the upper aperture of the tube.

It is important to remark that the light and the heat emitted by flames are by no means proportional to each other. The heat is due solely to the energy of the chemical action; and when a pure gaseous matter, without solid particles, composes both the burning body and the product of the combustion, little or no light

is emitted:—thus the flame of a jet of hydrogen is barely visible in clear daylight; and that of the oxyhydrogen jet itself, although one of the most intense sources of heat at our command, is scarcely more luminous than the flame of hydrogen. For the same reason the light of sulphur burning in oxygen is feeble, notwithstanding the intense energy with which they combine; both the vapour of sulphur and sulphurous acid are gaseous bodies. Phosphorus and chlorine, though they unite so energetically as to take fire at ordinary temperatures by mere contact, yet emit but little light during their combustion; the chlorides of phosphorus, as well as phosphorus itself, being very volatile bodies.

In all luminous flames the light is emitted from solid particles highly ignited. The light from bodies feebly ignited is red; as the temperature rises the light becomes yellow, then white, and when the heat is very intense, the more refrangible rays of the spectrum predominate, so that it has a shade of blue or violet.

By introducing a solid object into a non-luminous flame, a platinum wire, for example, into the oxyhydrogen jet, or, better still, a body which, like lime, does not melt at that temperature, the light becomes so intense that the eye can scarcely support it. Such bodies, however, since they do not contribute to the chemical changes occurring in the flame, necessarily reduce its heat, owing to their conducting power. It is immaterial whether the bodies so introduced be combustible, or have already undergone perfect combustion:—the flame of hydrogen may be rendered luminous either by blowing a little powdered charcoal through it, or by allowing finely powdered magnesia, oxide of zinc, or the white fumes of phosphoric acid produced by the combustion of phosphorus, to traverse it. Indeed no better illustration of this point can be given than is afforded by contrasting the painfully intense light produced by the combustion of phosphorus in oxygen, where the solid non-volatile phosphoric acid is produced, with the feeble light emitted by the same body as it burns in chlorine.

The flames used for illuminating purposes are all produced by the combustion of compounds of carbon and hydrogen. All of them, notwithstanding the perfect transparency of the gas before combustion, contain solid particles of carbon during the act of combustion. The separation of carbon during the process of combustion is seen by the simple expedient of introducing a cold body, such as a plate of metal, or a piece of glass, into a luminous flame; it becomes speedily blackened from the deposition of carbon.

The flame of a candle is sustained by the decomposition of the melted wax or tallow absorbed by the wick, and its conversion into

gaseous hydrocarbons by the heat of the combustion. At the lower part of the flame, *a*, fig. 297, these hydrocarbons are immediately mingled with atmospheric air, no separation of carbon occurs here, and they burn with a pale blue light. The greater portion of the combustible gases and vapours, however, are still unburned; they rise above the wick, forming the central dark part, *c*, of the flame: here they are subjected to a high temperature from the combustion of the blue portion already mentioned; the heat now causes the separation of the carbon in the solid form, which becomes intensely ignited in the burning gas, emitting light in the part marked *b*; and this carbon itself, in a properly adjusted flame, gradually burns away without residue or smoke, as it comes to the surface, *d*, and meets with oxygen. In order to produce the maximum amount of light, the point which requires the greatest attention is the due adjustment of the supply of air; if too much be given, the gas burns with a blue, feebly luminous flame; an effect which may be seen by blowing upon a common gas flame, or by watching the effects of the wind upon the exposed gaslights at night: the lengthening of the chimney of a lamp produces a similar effect. In these cases the gas becomes immediately mixed with the oxygen of the air, and it is completely burned before it has been exposed to an elevated temperature for a time sufficiently long to allow of the separation of carbon. The supply of air, however, must not be too much limited; otherwise, as may be seen by closing the central tube which admits air to an argand burner, the light becomes red from the reduction of temperature, the carbon passes off unburned, and the oxygen being insufficient to complete the combustion, the flame becomes smoky. The light of a flame is increased by any contrivance which, without deranging the order of the combustion, concentrates it into a smaller space, so as to raise the temperature of the deposited carbon to the maximum. It is in this way that an argand burner produces a far greater amount of light with a given consumption of gas, than if the same quantity of gas were burned in separate jets.

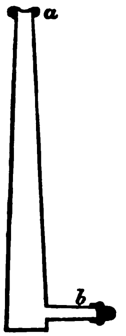
FIG. 297.

(404) *Theory of the Blowpipe.*—The temperature of a flame may be very materially increased by augmenting the activity of the combustion, and concentrating its effect by diminishing the extent of surface over which it would otherwise take place. It is upon this principle that all blowpipes act: a jet of air or of oxygen is thrown into the interior of a flame; the combustion is thus rendered

more rapid, it is limited to a much smaller space, and is entirely changed in character.

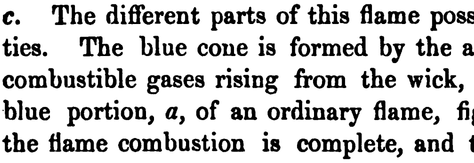
The mouth blowpipe is one of the most valuable and portable instruments of research which the chemist possesses: he is enabled by its means, in a few minutes, to arrive with certainty and economy at results which without its aid would require much expenditure both of fuel and of time; and it often affords information which could be obtained in no other way.

FIG. 298.



The mouth blowpipe consists essentially of a bent tube, terminating in a fine uniform jet, with a chamber for the condensation of moisture from the breath. A very convenient form of the instrument is shown at fig. 298. It consists of a conical tube of tin plate, about eight inches long, open at the narrow end, *a*, which is rounded off so as to adapt itself to the lips, and closed at its lower end, from the side of which projects a brass tube, *b*, about an inch in length, upon which is fitted a small brass jet. This jet is inserted to a short depth into the flame of a candle, about an eighth of an inch above the wick; when a current of air from the blowpipe is directed horizontally along the surface of the wick, the flame loses its luminosity, and is projected laterally in the form of a beautiful pointed cone, in which three parts are distinctly discernible (see fig. 299). In the centre is a well-defined blue cone; outside that is the brilliant part of the flame, terminating at *a*, and exterior to that is a pale yellow flame, *c*. The different parts of this flame possess very different properties. The blue cone is formed by the admixture of air with the combustible gases rising from the wick, and it corresponds to the blue portion, *a*, of an ordinary flame, fig. 297. In this part of the flame combustion is complete, and the oxygen introduced by the jet is in excess; the points where the excess of oxygen is absorbed by combination with fresh portions of the combustible vapours which are constantly rising from other parts of the wick, are clearly defined by the surface which seems to limit the blue cone. In front of this blue cone is the luminous portion, containing unburned combustible gases at a high temperature, which of course have a powerful tendency to combine with oxygen.

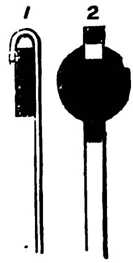
FIG. 299.



If a fragment of some metallic oxide, such as oxide of copper, sufficiently minute to be completely enveloped by the luminous portion, be introduced into this part of the flame, the oxide will be deprived of oxygen, in consequence of the superior affinity of the hot gases for this element, and the oxide will be reduced to the metallic state: hence this portion is termed the *reducing flame* of the blowpipe. At the apex, *c*, of the flame, the effects are reversed. Here, atmospheric oxygen at a high temperature is mechanically carried forward along with the completely formed products of combustion, and a fragment of any metal, such as lead, copper, or tin, if placed at this point will quickly become coated with oxide; and hence this spot is termed the *oxidating flame* of the blowpipe. A good illustration of the opposite actions of these contiguous portions of the flame is afforded by the effects which they respectively produce on a piece of flint-glass tubing. The silicate of lead contained in the glass is partially decomposed in the reducing flame, and the glass at this point becomes black and opaque from the reduction of the oxide of lead to the metallic state, but by placing the blackened part for a few seconds in the oxidating flame, oxygen is again absorbed by the metal, and the transparency of the glass is restored.

(404 *a*) *Use of the Mouth Blowpipe.*—The art of maintaining a continual blast by the mouth blowpipe is not easily described, but it can be acquired by practice without much difficulty. When a substance is to be examined by the blowpipe, it may be first heated alone in a small glass tube, in order to observe whether it melts or decrepitates, or is volatilized wholly or partially. It may next be heated in a narrow tube, open at both ends, to ascertain whether it burns, or changes colour, or emits any odour. It should then be ascertained whether it is reduced to the metallic state, and if it be reduced, what is the colour of the metal; whether it fuses easily, and whether it is brittle, crystalline, or malleable. These observations upon reduction may be best made when the globule is exposed to the flame upon a disk of charcoal, which may be conveniently supported, as proposed by Mr. Griffin, in the manner shown at 1 fig. 300, which represents an edge view of a slip of tin plate, about 8 inches long and half an inch wide, bent at one end so as to hold the charcoal disk. No. 2 shows it in front. The charcoal should be sawn into slices about the third of an inch in thickness, so as to present a surface across the grain. A small cavity should be formed upon the upper surface of each

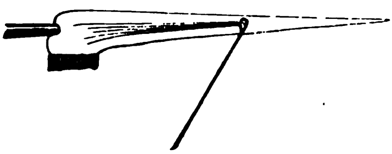
Fig. 300.



disk for the reception of the fragment of material under examination, which should be about the size of a pin's head, or a grain of mustard-seed.

Sometimes when the substance is not easily reducible, a platinum wire bent into a hook at one extremity forms a more convenient support, as shown at fig. 301. It may by this means be ascertained whether the substance imparts any colour to the flame; whether the body, if it be fusible, yields a transparent, an opaque, or a coloured bead; whether any change be produced in the substance, according as it is heated in the reducing or in the oxidating flame.

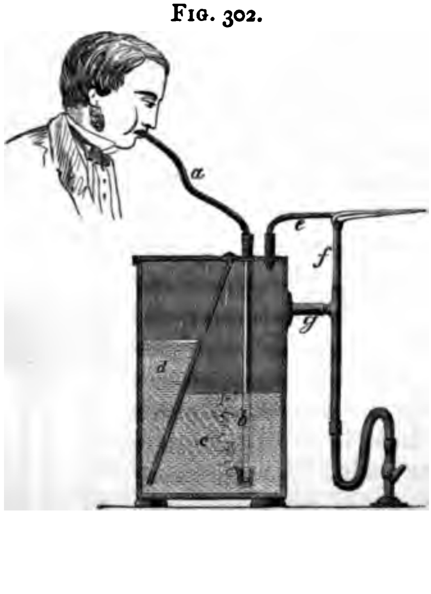
Fig. 301.



The employment of certain fluxes often aids the judgment of the operator by the colour or appearance thus produced. The most important of these fluxes are borax and carbonate of soda. When borax is used (494) a platinum wire forms the best support; but when carbonate of soda is employed, especially for the purpose of reducing the metals, a support of charcoal is required.

Different forms of the blowpipe have been proposed, according to the purposes for which it is destined. The glass-worker usually requires a large supply of air to be maintained uninterruptedly for long periods, and he commonly employs a pair of double bellows, worked by the foot.

Fig. 302.



A portable blowpipe for glass working may be made as follows:—A rectangular box of zinc, fig. 302, about 14 inches high and 6 wide, is divided into two chambers, *c* and *d*, by a diaphragm which passes obliquely nearly to the bottom of the box; these chambers communicate with each other below; one of them, *d*, is open above, and is covered with a loose lid; the other chamber, *c*, is closed at the top: a blowpipe jet, *e*, passes just

through the covering of this chamber, which is further supplied with a longer pipe, *a b*, passing down to within a short distance of the bottom, covered with a flap of silk to prevent the return of the water in case the operator should suddenly cease to blow through *a*. If the box be now partially filled with water, the pressure of the column of liquid will expel the air through the jet, *e*, in any desired direction. By blowing down the long pipe, the operator can renew the supply of air as often as may be necessary; it bubbles up into the closed chamber, *c*, driving the water back into the open one, when the column of liquid, by its pressure, renews the blast as before. The gas-burner, *f*, can be raised or lowered as may be necessary, and by means of a sliding joint, *g*, can be made to approach towards or recede from the jet, *e*, as may be required. An oil-lamp may be used when gas is not at hand; it has, indeed, the advantage of giving a more intense heat than gas, and it is less likely to reduce the oxide of lead contained in flint glass.

Where a very intense heat is required, a spirit-lamp, or gas-flame, through which a current of oxygen from a gas-holder is directed, may be employed; and occasionally, in cases where a still stronger heat is requisite, recourse may be had to the oxyhydrogen blowpipe, in which, owing to the complete intermixture of the two gases, the flame is solid, and therefore of small dimensions.

(405) Oil Gas, *Tetrylene* or *Butylene* ($C_8H_8=56$): *Sp. Gr. of Gas*, 1·854; *of Liquid* at 54°, 0·627; *Comb. Vol.* 4.—This compound was discovered by Faraday to be one of the constituents of the gases obtained by the destructive distillation of oil. It is almost insoluble in water, but is taken up freely by alcohol, and still more abundantly by oil of vitriol. Oil gas is condensed at 0° F. to a colourless liquid; the gas itself is colourless, and burns with a white, powerfully luminous flame. It contains the same proportions of carbon and of hydrogen as olefiant gas, but the two elements are condensed in oil gas into half the bulk which they occupy in olefiant gas. 1 volume of this gas requires 6 times its bulk of oxygen for its complete combustion, water and carbonic acid being the products. Consequently its composition may be thus represented:—

			By weight.		By vol.		Sp. gr.
Carbon	C_8 =	48 or	85·71	16 or	4	=	1·658
Hydrogen	H_8 =	8	14·29	16	4	=	0·276
Oil gas	C_8H_8 =	56	100·00		4	1 =	1·934

§ III. Compounds of Carbon with Oxygen.

Besides carbonic oxide and carbonic acid, carbon forms several other oxides possessed of acid characters: viz.,

Oxalic acid	$2\ HO,C_4O_6$
Rhodizonic acid	$3\ HO,C_7O_7$
Croconic acid	HO,C_5O_4
Mellitic acid	$2\ HO,C_8O_6$

(406) Oxalic Acid ($HO, C_2O_3+2\ Aq$), or, more properly, $2\ HO, C_4O_6+4\ Aq$.—This important and powerful acid may be usefully introduced here, though it belongs to the division of organic chemistry, as it is always obtained from sugar, starch, or some other substance of organic origin, and is one of the products of the oxidation of these substances under the influence of hot nitric acid or of hydrate of potash; it is moreover a frequent constituent of the juices of plants. Oxalic acid is abundant in the leaves of the wood sorrel (*Oxalis acetosella*), to which it communicates their powerfully acid taste, and in which it occurs in combination with potash as binoxalate of potash. It is found likewise in the *Rumex acetosa* and in the leaf-stalks of the common rhubarb. Many lichens owe their solidity to the presence of oxalate of lime, and have even been employed as a source of the acid. It is also contained abundantly in the barilla plant, in the form of neutral oxalate of soda.

Preparation.—Oxalic acid may be procured by heating tartaric, citric, or malic acid with an excess of hydrate of potash; and when starch, sugar, or ligneous tissue is similarly treated, hydrogen is evolved and oxalate of potash is among the products. Large quantities of oxalic acid are indeed now made for the calico printer by heating sawdust with hydrate of potash, or hydrate of soda. But the acid is commonly prepared by the oxidation of sugar or of starch by nitric acid. Berzelius recommends Schlesinger's mode of operating, as yielding it in the purest condition and in the largest quantity:—1 part of dry loaf sugar is dissolved in $8\frac{1}{4}$ parts of nitric acid, of sp. gr. 1·38, and heated in a flask until all effervescence has ceased; a copious evolution of carbonic acid and of nitric oxide attends the reaction. The solution is then evaporated by a water-bath to one sixth of its bulk, and the acid crystallizes on cooling. The mother-liquor may be further concentrated by evaporation: the oxalic acid is purified by recrystallization, and amounts to more than half the weight of the sugar employed.

Properties.—Oxalic acid as thus obtained crystallizes in trans-

parent four-sided prisms, which are represeuted by the formula ($2\ HO, C_4O_6 + 4\ Aq$). This acid requires about 9 parts of cold water for solution, but it is dissolved much more freely by boiling water; it is also soluble in alcohol. The crystals when heated to 212° become opaque, and lose 28·5 per cent. of water. The residue then consists of ($2\ HO, C_4O_6$), but the remaining 2 atoms of water cannot be expelled by the mere action of heat; they can only be displaced by an equivalent amount of some metallic oxide. If the dried crystals be placed in a retort, and heated by means of an oil-bath to between 300° and 320°, they are slowly sublimed and are condensed in white needles; but if heated above 320° the acid is decomposed. When the crystallized oxalic acid is heated quickly without previous desiccation, it melts in its water of crystallization, and at 311° is resolved, with apparent ebullition, into a mixture of carbonic acid, carbonic oxide, water, and formic acid:—

$$\overbrace{2\ HO,C_4O_6 + 4\ HO}^{\text{Oxalic acid.}} = 2\ CO_2 + 4\ HO + \overbrace{HO,C_2HO_3}^{\text{Formic acid.}}$$

and formic acid when decomposed by heat yields carbonic oxide and water;

$$HO,C_2HO_3 \text{ becoming } 2\ HO + (CO)_2$$

Berthelot has shown that this conversion of oxalic into formic acid is easily effected by dissolving the oxalic acid in glycerin, and heating to about 300°, when formic acid slowly passes over, and carbonic acid escapes; but if the temperature be raised to 380° carbonic oxide is obtained in abundance (1173).

The composition of oxalic acid is as follows:—

	Anhydrous.		Hydrated.		Crystallized.	
Carbon	$C_4 = 24$ or	33·3	$C_4 = 24$ or	26·6	$C_4 = 24$ or	19·05
Oxygen	$O_6 = 48$	66·7	$O_6 = 48$	53·4	$O_6 = 48$	38·10
Water			$2\ HO = 18$	20·0	$6\ HO = 54$	42·85
Oxalic acid	$C_4O_6 = 72$	100·0	$2\ HO, C_4O_6 = 90$	100·0	$2HO, C_4O_6, 4Aq = 126$	100·00

The solution of oxalic acid has an intensely sour taste; if swallowed, the acid acts as a powerful poison, occasioning death in a very few hours. The best antidote in such a case is the administration of chalk or of magnesia suspended in water.

It is a general rule that when an elementary body forms two or more acids with oxygen, the acid which contains the largest amount of oxygen is the most energetic in its action. Thus the sulphuric acid is more powerful than the sulphurous: chloric acid is stronger than hypochlorous acid, and the perchloric acid is stronger than either. It is, however, otherwise in the case of oxalic acid; although oxalic acid contains a smaller proportion of

oxygen than carbonic acid, its affinity for bases is much more energetic, and it decomposes all the carbonates with effervescence. The cause of this remarkable exception to the general rule has not hitherto been explained. Berzelius suggests that the carbon in oxalic acid may be in a different allotropic condition to that in which it exists in carbonic acid. The equivalent of carbon in oxalic acid might therefore be $C=12$, or the double of what it is in carbonic acid; and oxalic acid might thus be a teroxide of a particular form of carbon, CO_3. On the other hand, the facility with which oxalic acid, under the influence of sulphuric acid (303), is decomposed into a mixture of equal volumes of carbonic acid and carbonic oxide, renders such a hypothesis very doubtful. Some chemists have been disposed to regard the oxalic acid rather as an oxide of carbonic oxide $(CO)_2O$, than as a true oxide of carbon. Such speculations, however, are valuable rather on account of the experiments and researches which they suggest, than from any inherent probability which they possess.

Oxalates.—Until lately oxalic acid was regarded as monobasic; but Gerhardt has given good reasons for viewing it as dibasic. It forms a large number of insoluble salts. The insolubility of oxalate of lime in water has led to the employment of oxalic acid as a reagent for indicating the existence of lime in solution, and for determining its amount. On adding a neutral oxalate to a neutral or alkaline solution of any salt of lime, the oxalate of lime falls as a white precipitate, which is insoluble in acetic acid. After drying at 100° F., 100 parts of this salt consist of, $2\,CaO,C_4O_6 + 4\,Aq$, and when heated to bright redness leave 34·15 of pure quicklime, corresponding to 43·9 of anhydrous oxalic acid. The oxalates of magnesia, cadmium, and manganese are also white and nearly insoluble: they each, when dried at 212°, retain 4 Aq. Oxalate of zinc is white; oxalate of cobalt is rose-coloured; oxalate of nickel is greenish white, and the protoxalate of iron is yellow: they are all sparingly soluble, and retain 4 Aq at 100° F. The oxalates of baryta and strontia are white, and that of copper is of a pale blue: they are nearly insoluble, and retain 2 Aq at 212°. The oxalates of lead and silver are white, and anhydrous. All the insoluble oxalates are readily dissolved by diluted nitric acid.

An insoluble basic oxalate of lead $(6\,PbO, C_4O_6)$ may be obtained by precipitating the tribasic acetate of lead by means of a neutral soluble oxalate. One of the most characteristic salts of this acid is the oxalate of silver, which when heated on platinum foil is suddenly reduced to the metallic state, and is dispersed with a slight explosion, owing to the sudden liberation of carbonic

acid; $2\ AgO,C_4O_6 = 2\ Ag + 4\ CO_2$. The oxalates of many other of the metals which have but small affinity for oxygen, those of cobalt and nickel among the number, are reduced to the metallic state if heated to redness in a closed vessel, so as to exclude atmospheric oxygen; 4 equivalents of carbonic acid gas being expelled, whilst the pure metal is left behind. This reducing action occurs in the case of gold, when a solution of a salt of this metal is simply boiled with an oxalate; the gold is precipitated, either in flakes or in the form of a very finely divided powder. The oxalates of the alkalies and the alkaline earths are converted by a dull red heat into carbonates of these bases; the carbonic oxide burning off with a pale blue flame, whilst the salt does not exhibit any appearance of charring.

With the alkalies oxalic acid forms three classes of salts: one class, the normal salts of the acid, contains 2 equivalents of base to 2 equivalents or 1 atom of the acid; such, for example, is the case with the oxalate of ammonia ($2\ H_4NO,C_4O_6 + 2\ Aq$). The second class is acid, and contains 1 equivalent of a fixed base and 1 of water to 2 equivalents or 1 atom of the acid; binoxalate of potash or the salt of sorrel ($KO, HO, C_4O_6 + 2\ Aq$), is a salt of this description: whilst the third class, exemplified by the salt usually termed quadroxalate of potash ($KO, 3\ HO, 2\ C_4O_6 + 4\ Aq$), contains the unusual proportion of 4 equivalents or 2 atoms of a dibasic acid to 1 atom of a fixed base and 3 atoms of basic water.

Oxalic acid forms a large number of double salts,—such as that of protoxide of uranium and ammonia (UO, H_4NO, C_4O_6), that of sesquioxide of uranium and ammonia ($U_2O_3, H_4NO, C_4O_6 + 6\ Aq$), and a beautiful series of salts with oxide of chromium, of which the double salt of potash ($3\ KO, Cr_2\ O_3, 3\ C_4O_6 + 6\ Aq$) is the representative.

(407) *Rhodizonic, Croconic, and Mellitic Acids.*—Three other acids containing carbon and oxygen are known under these names, but they are of slight importance.

Rhodizonic Acid ($3\ HO, C_7O_7$?) is an acid which forms salts of a beautiful red or scarlet colour, whence it derives its name (from ῥόδον, a 'rose'). It is obtained by the action of a moist atmosphere on the dark olive-green compound which potassium yields when gently heated in carbonic oxide gas, and which is formed abundantly during the preparation of potassium.

If the aqueous solution of rhodizonate of potash be boiled, it is decomposed into oxalate of potash, and the salt of a new acid, which from the yellow colour of its compounds is termed *Croconic acid*, whilst potash is set at liberty (Liebig):—

$$2\,HO + 2\,\underbrace{(3\,KO,C_7O_7)}_{\text{Rhodizonate of potash.}} = \underbrace{2\,KO,C_4O_6}_{\text{Oxalate of potash.}} + \underbrace{2\,(KO,C_5O_4)}_{\text{Croconate of potash.}} + \underbrace{2\,(KO,HO)}_{\text{Potash.}}$$

Croconic acid is obtained by decomposing croconate of potash with silicofluoric acid. It forms yellow crystals soluble both in water and in alcohol. Croconic acid and the soluble croconates furnish yellow sparingly soluble crystalline plates when mixed with salts of baryta or of lead.

Mellitic Acid ($2\,HO, C_8O_6$) has hitherto been found only in *Mellite*, a rare mineral, consisting of mellitate of alumina ($2\,Al_2O_3, 3\,C_8O_6+36\,Aq$), which is now and then met with in lignite, and occurs crystallized in honey-yellow transparent octohedra. Mellitic acid is extracted from mellite by boiling the powdered mineral with carbonate of ammonia. Mellitate of ammonia is obtained in solution: by the addition of acetate of lead to the liquid, the mellitate of lead ($2\,PbO,C_8O_6+2\,Aq$) is precipitated. This precipitate, when washed, is suspended in water and decomposed by a current of sulphuretted hydrogen; sulphide of lead is thus formed, and is separated by filtration from the solution which contains the liberated mellitic acid: on evaporating the liquid the acid is left in a state of purity. Mellitic acid is soluble in water and in alcohol; it may be obtained crystallized in groups of needles by the spontaneous evaporation of the alcoholic solution. Its solution reddens litmus strongly, and has a strongly sour taste. Mellitic acid is unchanged by boiling nitric or sulphuric acids. The acid is decomposed by heat into a volatile crystalline sublimate, and into carbon. With the salts of lead the mellitates give a voluminous white precipitate, which gradually shrinks in bulk and becomes crystalline.

§ IV. Compounds of Carbon with Nitrogen.

(408) Cyanogen (NC_2 or $Cy=26$): *Sp. Gr.* 1·8064; *Comb. Vol.* 2.—This substance is one of the most interesting compounds of carbon, and its discovery by Gay-Lussac, in 1814, formed an epoch in the history of chemical science. It was the first compound body which was distinctly proved to enter into combination with elementary substances in a manner similar to that in which the elements combine with each other. New views of chemical composition were thus originated, which have since acquired an extensive development, and have exercised a most material influence upon the theory of organic compounds in general. The name of *Cyanogen* (from κύανος 'blue,' γεννάω to 'produce'), is derived from

the circumstance that this body forms an essential ingredient in Prussian blue. Its components are united in the proportion of 2 atoms of carbon and 1 atom of nitrogen, but no direct union of these elements can be effected. If a mixture of charcoal and carbonate of potash be heated to redness in a porcelain tube, and nitrogen be passed over it, the potash is reduced to potassium, carbonic oxide escapes abundantly, whilst cyanogen is formed and unites with the potassium, yielding cyanide of potassium :—

$$KO, CO_2 + 4\,C + N = K,NC_2 + 3\,CO.$$

Cyanogen is also present in small quantity among the products obtained during the distillation of pit coal; and it is furnished during the decomposition of oxalate of ammonia by heat, $2\,H_4NO, C_4O_6$ becoming $2\,C_2N + 8\,HO$.

The compounds of cyanogen are, however, almost always obtained from the double cyanide of potassium and iron, a salt which crystallizes in transparent yellow tables, and is commonly known by the name of *prussiate of potash*, or ferrocyanide of potassium. This salt is prepared by heating, in a covered iron pot, about 5 parts of refuse animal matter, such as the parings of hoofs, hides, horns, &c., with 2 parts of pearlash, and iron filings ; the nitrogen and carbon of the animal matters react upon each other at a high temperature, and combine with a portion of reduced potassium and with iron. On digesting the mass, when cold, with water, the ferrocyanide of potassium ($K_2,FeCy_3 + 3Aq$) is formed, and is deposited from the solution in large four-sided tables. When 10 parts of this salt are dissolved in 4 times their weight of warm water, and distilled with 7 parts of oil of vitriol diluted with twice its weight of water, until about half the bulk of the liquid has passed over, a dilute solution of hydrocyanic acid (HCy) is formed ;* this, if saturated with red oxide of mercury, furnishes, on evaporation, a crystallizable compound, the cyanide of mercury (HgCy). If this be thoroughly dried, and heated in a retort, it is decomposed into mercury, which distils over, and cyanogen, which passes off as a permanent gas.

Cyanogen is a transparent colourless gas, of a peculiar, penetrating odour : it is poisonous if respired. It burns with a beautiful flame edged with purple. Cyanogen is soluble in one fourth

* The reaction in this case is rather less simple than might have been anticipated ; it was first accurately traced by Everitt :—

$$2\,(K_2FeCy_3) + 6\,(HO, SO_3) = 3\,HCy + (KFe_2Cy_3) + 3\,(KO, HO, 2\,SO_3).$$

Half the cyanogen only is expelled as hydrocyanic acid, the other half remaining behind in the form of a white, insoluble, double cyanide of iron and potassium (KFe_2Cy_3).

of its bulk of water, and still more freely so in alcohol; hence it must be collected over mercury. In porcelain or glass vessels it supports a high temperature without decomposition, but if heated in iron tubes, charcoal is deposited, and a volume of nitrogen, equal to that of the cyanogen used, remains.

The composition of cyanogen may be determined by detonation in the eudiometer with oxygen; the combustion is attended with a powerful explosion. Two volumes of cyanogen with 4 volumes of oxygen yield 4 volumes of carbonic acid and 2 volumes of nitrogen; 4 volumes of carbon vapour and 2 volumes of nitrogen must therefore be condensed in it into 2 volumes, as is shown in the following table:—

		By weight.		By volume.		Sp. gr.
Carbon	C_2	= 12	or 46·15	4	or 2	= 0·829
Nitrogen	N	= 14	53·85	2	1	= 0·971
Cyanogen	NC_2	= 26	100·00	2	1	= 1·800

Cyanogen is readily reduced to the liquid state by a pressure of its own vapour equal to about 4 atmospheres. It forms a colourless, limpid liquid, of sp. gr. 0·866 at 63°, which, on the removal of the pressure, rapidly but quietly resumes the gaseous state. It freezes at —30°, and forms a transparent crystalline solid, which is nearly of the same density as the liquid.

Fig. 303 shows an easy method of liquefying cyanogen: a tube of hard glass is bent into the form *a, b, c*. Into the limb, *a*, well dried cyanide of mercury is introduced; heat is applied to the cyanide of mercury at *a*; the bend, *b*, is placed in a basin containing a freezing mixture of ice and salt; as soon as the gas begins to escape, the stopcock at *c* is closed, and liquid cyanogen becomes condensed in the bend, *b*.

FIG. 303.

If potassium be heated in cyanogen it burns and combines with it, without occasioning the decomposition of the gas, forming a saline body analogous to common salt. This experiment shows the existence of the remarkable property possessed by cyanogen, of

combining with metals and other bodies like an element. This peculiarity in the mode of combination of cyanogen, which has given rise to the theory of compound radicles now so extensively applied in organic chemistry, will be better traced by examining a few of the numerous compounds which cyanogen forms with the elementary bodies.

(409) HYDROCYANIC OR PRUSSIC ACID ($HCy=27$): *Sp. Gr. of Vapour*, 0·9476; *of Liquid*, 0·7058 *at* 45° *F.*; *Melting Pt.* 5°; *Boiling Pt.* 80°; *Comb. Vol.* 4.—Cyanogen forms with hydrogen a highly important compound, though the two bodies cannot be made to unite directly with each other. If a current of dried sulphuretted hydrogen be transmitted through a long tube filled with cyanide of mercury until the cyanide has become nearly blackened throughout, sulphide of mercury and hydrocyanic acid are formed; but it may also be prepared by decomposing any of the cyanides by a strong acid, and subjecting them to distillation. The most economical process is that of Wöhler: he prepares a crude cyanide of potassium by fusing 8 parts of the dried yellow ferrocyanide of potassium with 3 of carbonate of potash and 1 part of charcoal. In this reaction the potash of the carbonate is deprived of oxygen by the charcoal, and the potassium takes the place of the iron in the ferrocyanide; 3 atoms of cyanide of potassium being formed from each atom of ferrocyanide; the carbonic acid of the carbonate of potash is also reduced to the state of carbonic oxide by the excess of charcoal which is employed. This decomposition is shown in the following equation:—

$$K_2FeCy_3 + KO,CO_2 + 2\ C = 3\ KCy + Fe + 3\ CO.$$

The fused mass is treated with 6 times its weight of water, in a well closed vessel; the clear liquid is decanted from the iron which it is the object of this operation to separate, and is poured into a retort: sulphuric acid, diluted with an equal weight of water, is gradually added in the proportion of 1 part of oil of vitriol to 2 parts of the cyanide. At first the distillation proceeds spontaneouly from the heat developed by the admixture of the sulphuric acid with the water. In order to condense the acid, the products are made to pass through a long U-shaped tube, immersed in cold water, and filled with chloride of calcium, with the exception of the first fourth of the tube, which contains fragments of the crude cyanide of potassium; to the bent tube is attached a second delivering tube, which passes to the bottom of a bottle cooled with ice and salt. The chloride of calcium in the syphon tube retains the moisture, and the cyanide of potassium absorbs any sulphuric

acid that might chance to pass over, whilst the hydrocyanic acid collects in an anhydrous state in the cooled receiver. The reaction of sulphuric acid upon cyanide of potassium is very simple, being exactly analogous to its action upon chloride of sodium :—

$$KCy + HO, SO_3 = HCy + KO, SO_3.$$

Anhydrous hydrocyanic acid is a colourless, transparent, and very volatile liquid; so rapidly does it evaporate, that if a drop be allowed to fall upon a glass plate, part of the acid becomes frozen by the cold produced by its own evaporation. Its vapour has an odour of peach blossoms, causing a peculiar sense of oppression, and of constriction in the fauces. Owing to its intensely poisonous character, the greatest care is requisite in conducting experiments upon this substance; the apparatus should always be arranged so that the vapours are carried away from the operator by a brisk current of air.

Hydrocyanic acid is very inflammable; it burns with a flame resembling that of cyanogen, but of a whiter colour. In conformity with its analogy with the hydrogen acids of chlorine and the other halogens, it is composed of 2 volumes of hydrogen and 2 of cyanogen united without condensation. If 5 volumes of oxygen be mingled with 4 volumes of this vapour, a mixture is obtained which detonates powerfully on transmitting the electric spark through it; 4 volumes of carbonic acid and 2 volumes of nitrogen remain, and 2 volumes of steam are condensed. The composition of hydrocyanic acid may be calculated from the result of this experiment, and may be represented as follows :—

			By weight.		By volume.		Sp. gr.
Carbon	C_2	= 12	or 44·45	4	or 1·0	=	0·414
Nitrogen	N	= 14	51·85	2	0·5	=	0·485
Hydrogen	H	= 1	3·70	2	0·5	=	0·034
Hydrocyanic acid	H,NC_2	= 27	100·00	4	1·0	=	0·933

The acid properties of this compound are but feeble; it reddens litmus slightly, dissolves red oxide of mercury freely, and precipitates nitrate of silver in white flocculi (AgCy). Cyanide of potassium always has an alkaline reaction: its solution emits the odour of the acid. Pure hydrocyanic acid may be kept unchanged if excluded from light; but in diffused light it becomes decomposed, and a brown matter, consisting chiefly of paracyanogen, is formed. Pelouze has pointed out a remarkable decomposition which furnishes dilute hydrocyanic acid almost in a state of purity: crystallized formiate of ammonia contains the elements of 1 equivalent of hydrocyanic acid and 4 equivalents of water. If this salt be

placed in a retort and heated, it melts at 248°, loses a little ammonia at 284°, and between 356° and 392° distils over, and if the vapour be transmitted through a red-hot tube it is wholly converted into hydrocyanic acid and water; $H_4NO,C_2HO_3 = HNC_2 + 4\ HO$. If equal measures of concentrated hydrocyanic and hydrochloric acids be mixed together, formic acid and ammonia are reproduced.

Hydrocyanic acid, mixed with a peculiar essential oil, is obtained by distillation from the kernels of the bitter almond, and from those of many varieties of stone fruit: it is also present in the water which is distilled off the leaves of the laurel, the peach, and some other shrubs: the juice of the tapioca plant (*Jatropha manihot*) likewise contains it, and it is also formed under various circumstances during the oxidation and decomposition of some kinds of nitrogenized substances.

The preparation of diluted hydrocyanic acid by distillation of ferrocyanide of potassium with diluted sulphuric acid has been already noticed, but as the acid is now frequently employed in medicine, it is highly important, on account of its energetic action, to be able to insure its preparation of an uniform strength. This is easily attained by the process of the London Pharmacopœia, which directs 48½ grains of cyanide of silver to be suspended in an ounce of water, and to be decomposed by 39½ grains of hydrochloric acid, decanting the clear liquid from the chloride of silver; this acid contains 2 per cent. of the anhydrous acid. The dilute acid is less prone to decomposition than if concentrated, especially if a little free sulphuric acid be present: but it should always be excluded from the light. This acid is extremely volatile, and if a bottle containing the diluted acid be left open for a few hours it will be found to have suffered a very material reduction in strength; indeed the mere opening and closing the bottle in dispensing the medicine always reduces its strength. When subjected to distillation a large quantity is usually lost, and the greater portion of the acid comes over in the first fourth of the distillate. What is called *Scheele's acid* varies greatly in strength, owing to the difficulty of condensing the acid vapour. It is directed to be prepared by mixing 10 parts of ferrocyanide of potassium with 3·75 of oil of vitriol previously diluted with 40 parts of water, and distilling over till 10 parts are collected. It seldom contains more than 5 per cent. of the acid, and the proportion is often considerably less.

(410) *Cyanides.*—The cyanides of the alkaline metals are freely soluble in water. Many of the cyanides of the heavier metals are insoluble in water, but most of them are decomposed with evolu-

tion of hydrocyanic acid when boiled with hydrochloric acid; those of silver and mercury, when heated to redness, yield cyanogen gas. Solutions of the salts of the suboxide of mercury give a grey precipitate of the reduced metal; but the salts of the red oxide give no precipitate with the cyanides. Most of the cyanides which are insoluble in water may be dissolved by means of a solution of the cyanides of the metals of the alkalies, or of the alkaline earths: in such cases double cyanides are generally formed. Liebig has given a ready method for the exact determination of the strength of a solution of hydrocyanic acid formed upon the solubility of those double cyanides:—The acid to be tested is supersaturated with a solution of caustic potash, and a standard solution of nitrate of silver (17 grains of nitrate in 1000 measured grains of water) is gradually added, agitating the mixture after each addition; as soon as the precipitate is no longer redissolved, the number of divisions of nitrate added must be read off. 17 grains of the nitrate of silver represent 5·4 grains of hydrocyanic acid. The reaction is the following:—

$$AgO,NO_5 + 2\ KCy = KO,NO_5 + KCy,AgCy.$$

The presence of chlorides does not interfere with the application of the test. Sulphate of copper may be substituted for the nitrate of silver, if the hydrocyanic solution be rendered alkaline with ammonia instead of with potash. The reaction is complete as soon as the liquid acquires a slight blue tinge: 14·5 grains of the crystallized sulphate represent 5·4 grains of hydrocyanic acid.

The presence of the soluble cyanides, or of hydrocyanic acid in solution, may be determined by the following tests:—

1. With nitrate of silver a white, curdy precipitate, which does not blacken by exposure to light, is formed; it is nearly insoluble in cold nitric acid; when heated to redness it gives off the inflammable vapour of cyanogen.—2. If to the liquid a slight excess of potash be added, and then a mixture of protosulphate and persulphate of iron, a precipitate is occasioned which when treated with excess of hydrochloric acid leaves Prussian blue. This test may be modified by heating gently the suspected mixture with sulphuric acid, and suspending in the flask or retort for a few minutes, a piece of paper moistened with a solution of potash; on dropping a weak solution of protosulphate of iron upon the paper, and immersing it in diluted sulphuric acid, very minute traces of hydrocyanic acid may be recognised by the formation of Prussian blue.—3. Let the liquid be acidulated with a few drops of hydrochloric acid, place it in a watch glass, and let a second watch glass

moistened with a drop of a solution of hydrosulphate of ammonia be inverted over it; after a few minutes let the upper watch-glass be removed, the liquid be evaporated to dryness by steam heat, and let the dry residue be treated with a drop of a weak solution of sesquichloride of iron; a red sulphocyanide of iron is formed under these circumstances.

The cyanides of iron, of cobalt, of chromium, of platinum, and of some other metals, form, with the cyanides of the alkalies and of the earths, compounds of a peculiar character, in which the presence of the iron, or of the cobalt, &c., cannot be detected by the usual tests for these metals. Some of these compounds are of considerable importance, and will be noticed at a future point. (1346 and *seq.*)

(411) Cyanic Acid ($HO,CyO=9+34$).—If cyanogen gas be passed into an alkaline solution, a change ensues something analogous to that which occurs when chlorine is similarly treated, cyanide and cyanate of the base being produced; but the cyanic acid contains only 1 equivalent of oxygen united with 1 of cyanogen; $2\ Cy+2\ (KO,HO)=KCy+KO,CyO+2\ HO$.

Cyanate of potash, however, is better prepared in a state of purity, by fusing the cyanide of potassium in a crucible, and adding litharge (oxide of lead) in small quantities, till the oxide ceases to be decomposed; $KCy+2\ PbO=KO,CyO+2\ Pb$. The cyanate is easily separated from the reduced lead and the excess of oxide of lead, which, from their superior density, sink through the melted mass to the bottom. Another method of preparing the cyanate of potash consists in heating an intimate mixture of 2 parts of thoroughly dried ferrocyanide of potassium with 1 part of finely powdered anhydrous black oxide of manganese: the mixture is placed upon a sheet-iron plate and heated to dull redness, and the mass is kept constantly stirred. When the combustion has ceased, cyanate of potash may be dissolved out of the residue with hot alcohol, from which it crystallizes as the solution cools.

Cyanate of potash, if kept dry, may be preserved without change; but so unstable is the cyanic acid when uncombined with a fixed base, that on attempting to separate it from the cyanate of potash by the addition of sulphuric or any other acid, traces of it only are obtained: a brisk effervescence ensues,—each equivalent of the cyanic acid assimilates the elements of water, and is almost entirely resolved into 1 equivalent of ammonia, which remains in combination with the acid employed in decomposing the

cyanate, and 2 equivalents of carbonic acid, which escape with effervescence:—

$$2\,(\overbrace{HO,SO_3}^{\text{Sulph. Acid.}}) + \overbrace{KO,C_2NO}^{\text{Cyanate Potash.}} + 2\,HO = \overbrace{H_4NO,SO_3}^{\text{Sulphate ammonia.}} + \overbrace{KO,SO_3}^{\text{Sulph. Potash.}} + 2\,CO_2.$$

Cyanic acid may be otherwise procured: viz., by distilling *cyanuric acid* ($2\,HO,C_6N_3HO_4$), which is a crystallizable acid substance (1363), 1 atom of which contains exactly the same elements as 3 atoms of hydrated cyanic acid. When this compound is sealed up in a bent glass tube, one limb of which is kept cool whilst heat is applied to the cyanuric acid in the other limb, a limpid, colourless liquid distils over and is condensed. The cyanuric acid is thus wholly converted into pure hydrated cyanic acid.

Cyanic acid has an extremely pungent odour, and is very volatile; it acts as a powerful caustic if incautiously dropped upon the skin. It is, however, impossible to preserve this compound, for in the course of a few hours it changes spontaneously into a white enamel-like mass, which is permanent in the air, insoluble in water, and destitute of acid properties. To this body the name of *cyamelid* has been given: it has the same composition by weight as the hydrated cyanuric and cyanic acids.

Solutions of the soluble cyanates give white precipitates with solutions of the salts of lead, of silver, or of suboxide of mercury; they yield no precipitate with solution of corrosive sublimate, or with the solutions of salts of iron or of tin. With nitrate of copper they give a greenish-brown precipitate, and with terchloride of gold a brown precipitate.

(412) Fulminic Acid.—Besides the remarkable oxides of cyanogen already mentioned, there is another acid which yields on analysis the same per-centage of its components as cyamelid, and the cyanic and cyanuric acids, though it possesses properties totally different from any of them. Its compounds explode with fearful violence. By dissolving 1 grain of silver in 20 grains of nitric acid diluted with about 50 of alcohol, the new compound is deposited in crystals, which, when dry, detonate with the slightest friction: they consist of $2\,AgO,N_2C_4O_2$. The reaction by which this salt is produced is complicated; the nitrogen, however, is derived from the nitric acid, and the carbon from the alcohol.

Fulminic acid has not been obtained in an isolated form; on attempting to separate it from its salts by a more powerful acid it is resolved into hydrocyanic acid and other bodies. Allusion

will again be made to the fulminates when other compounds of cyanogen are described (1364).

When the fulminates are boiled with a solution of chloride of sodium, or of chloride of potassium, the acid is converted into another isomeric compound termed *isocyanuric* or *fulminuric acid* (1364). This body is but very slightly explosive.

(413) *Isomerism.*—The properties of these oxides of cyanogen serve clearly to show that mere identity in ultimate composition is not sufficient to produce identity of chemical character or properties; they place the doctrine of *isomerism* (or the existence of compounds identical in ultimate composition, but different in chemical properties) in a striking point of view. Numerous other instances will occur as we pursue further the study of the different compounds, not only of cyanogen, but of other bodies, and particularly of those which form the subject of organic chemistry.

There are various forms of isomerism; in some cases we have no clue to the probable differences of molecular arrangement: in others there is every reason to suppose that the arrangement of the elementary molecules is on a totally different plan in the two bodies which are compared. Hydrated cyanic acid, for instance, may be represented as hydrated oxide of cyanogen; whilst it is certain that in cyamelid, which is insoluble, and presents nothing of the acid character, the arrangement of its constituents is quite different. Isomeric compounds, the equivalent numbers of which are identical, are said to be *metameric*. In other cases, the differences in properties of bodies which contain equal amounts of their constituents in 100 parts, may be simply explained upon the supposition that in the different compounds the state of condensation of these elements is different; bodies supposed to be thus constituted have been termed *polymeric*.

The following table contains a list of several different polymeric compounds of carbon and hydrogen which contain these two elements in the proportion of single equivalents of each. Each of these bodies, however, possesses properties peculiar to itself: and if equal volumes of the vapour of each be compared, it will be found that the elements have undergone different degrees of condensation in the different compounds. As the density of the vapour increases, it has been observed that the boiling point of such as are liquid rises proportionately. Supposing that an equivalent of each compound gives off 4 volumes of vapour, the formulæ will be such as are contained in the subjoined table:—

Substances.	Formula.	Density of vapour.		Boiling point, ° F.
		Observed.	Calculated.	
Methylene (?)	C_2H_2	0·490	0·483	
Olefiant gas (Ethylene) .	C_4H_4	0·978	0·967	
Propylene (Tritylene) .	C_6H_6	1·498	1·451	
Oil gas (Tetrylene) . .	C_8H_8	1·852	1·934	0
Amylene	$C_{10}H_{10}$	2·386	2·418	102
Caproylene (Hexylene).	$C_{12}H_{12}$	2·875	2·902	131
Heptylene	$C_{14}H_{14}$			122?
Naphthene (Octylene) .	$C_{16}H_{16}$	3·90	3·868	257
Eleene (Nonylene) . .	$C_{18}H_{18}$	4·48	4·351	
Paramylene	$C_{20}H_{20}$	5·061	4·836	320
Cetylene.	$C_{32}H_{32}$	8·007	7·736	527
Cerotylene	$C_{54}H_{54}$		12·159	
Melissine	$C_{60}H_{60}$		14·508	

In this series, olefiant gas has double the density of methylene, and hence it must contain in the same volume of vapour twice as many elementary atoms. In like manner oil gas must contain twice as many atoms as olefiant gas, and four times as many as methylène; naphthene will contain twice as many as oil gas, and cetylene again will contain double the number of atoms of carbon and hydrogen in the same volume of vapour as naphthene.

(414) Paracyanogen (N_2C_6?).—The ordinary operation of preparing cyanogen gas from cyanide of mercury affords a good illustration of polymeric isomerism. After the mercury and the cyanogen have been expelled from the glass retort, there always remains a certain quantity of a brown matter, composed of nitrogen and carbon, combined in the same proportions as in cyanogen. *Paracyanogen*, as this brown body is called, is insoluble in water; it is neither volatile nor fusible, but like cyanogen it enters into combination with other elementary bodies, though the composition of these compounds has been as yet but imperfectly studied.

In paracyanogen the carbon and nitrogen are more condensed than in cyanogen; so that if we regard cyanogen as composed of NC_2, paracyanogen, according to the experiments of Johnston, would consist of N_3C_6, its combining number being three times that of cyanogen, and the elements which compose it being more compactly united.

(415) Chlorides of Cyanogen.—Chlorine forms with cyanogen three polymeric compounds, all of which are highly poisonous: one is gaseous at the ordinary temperature of the air; the second is liquid, and the third is solid.

The *Gaseous Chloride of Cyanogen* ($CyCl = 61{\cdot}5$; *Sp. Gr.* 2·124) is colourless: it has an intolerably pungent odour, and irritates the eyes powerfully; at 0° F. it condenses in long prismatic needles, which fuse at 5°. Four volumes of the gas contain 2 volumes of chlorine and 2 of cyanogen, united without condensation, so that its composition may be thus represented:—

		By weight.		By volume.		Sp. gr.
Cyanogen	Cy =	26	or 42·28	2	or 0·5	= 0·900
Chlorine	Cl =	35·5	57·72	2	0·5	= 1·226
Chloride of Cyanogen	CyCl =	61·5	100·00	4	1·0	= 2·126

Gaseous chloride of cyanogen is freely soluble in water, in ether, and in alcohol; the solution has no acid reaction, and does not precipitate nitrate of silver. It is obtained readily by transmitting a current of chlorine through a retort containing a mixture of powdered cyanide of mercury and water cooled to 32° by immersion in melting ice: the chloride of cyanogen is dissolved by the water; from this solution it may be expelled by the application of a gentle heat, and may be collected over mercury. According to Persoz, the gaseous chloride of cyanogen, if liquefied under the pressure of its own vapour, and preserved in tubes hermetically sealed, gradually becomes converted into a crystallized mass of the solid chloride.

Liquid Chloride of Cyanogen ($Cy_2Cl_2 = 123$; *Melting Pt.* 19°; *Boiling Pt.* 61°) is procured by exposing cyanide of mercury to the action of chlorine gas in direct sunlight. A yellowish oily liquid is thus obtained, which is converted into a crystalline mass at 19°. It has an odour resembling that of the gaseous chloride. Liquid chloride of cyanogen is not soluble in water, but is freely soluble in alcohol.

Solid Chloride of Cyanogen ($Cy_3Cl_3 = 184{\cdot}5$); *Sp. Gr. of Vapour*, 6·39; *Melting Pt.* 284°; *Boiling Pt.* 374°.—This substance crystallizes in white needles. It has a disagreeable odour, like that of mice. The vapour of this compound is three times as dense as that of the gaseous chloride, it therefore contains 6 volumes of chlorine and 6 volumes of cyanogen condensed into the space of 4 volumes. This chloride is but sparingly soluble in water, though it is freely taken up by alcohol and by ether. The solid chloride of cyanogen may be prepared by decomposing concentrated hydrocyanic acid by exposing it in a glass vessel with an excess of dry chlorine to the direct rays of the sun.

Bromine and iodine form solid crystalline compounds with cyanogen, corresponding in composition with the gaseous chloride;

they may be obtained by distilling cyanide of mercury with bromine or with iodine.

(416) There are other important compounds of cyanogen, the consideration of which will be more advantageously pursued hereafter; it will be sufficient at this point to indicate some of their leading chemical peculiarities.

Cyanogen, as we have seen, enters into combination with the non-metallic elements as though it were of itself an elementary body. In this manner bodies such as the chlorides, the bromides, and the iodides of cyanogen may be obtained; they form well-defined compounds, which do not exhibit any special tendency to unite with other elements. In other cases, however, it is important to observe that many of the compounds to which cyanogen gives rise are themselves endowed with the property of uniting again, as though they were simple bodies, with other elements. With sulphur, for example, cyanogen forms a bisulphide (NC_2S_2), which, in combination with the metals, performs the part of a compound radicle, usually termed *sulphocyanogen* (Scy), and which produces a series of salts, termed sulphocyanides, many of which may be crystallized; of this the sulphocyanide of potassium, K,NC_2S_2 or K,Scy, furnishes an instance (1359). Similar compound radicles are furnished also by the union of cyanogen with many of the metals themselves; in this way iron in the *ferrocyanides*, and cobalt and chromium in the *cobalticyanides* and *chromicyanides*, form each a compound group, or salt-radicle, which, when it unites in its turn with other metals, performs the functions of a simple body, such as chlorine or iodine: an example of this is seen in the well-known prussiate of potash, or as it is usually termed, ferrocyanide of potassium, ($K_2,FeCy_3$), in which the compound of iron and cyanogen, $FeCy_3$, is considered as a compound radicle known as *ferrocyanogen*, (Fcy).

§ V. General Remarks on the Discrimination of the Gases from each other.

(417) Having now described all the gaseous compounds which are of any considerable importance, with the exception of two—viz., arseniuretted hydrogen and antimoniuretted hydrogen, it will be advantageous to take a brief review of their general characters before passing to the consideration of the metals and their compounds.*

There are about 30 bodies which are permanently gaseous at the mean temperature of the atmosphere. Several of these compounds are met with in the uncombined form in the atmosphere, either uniformly, or under particular circumstances not of unfrequent occurrence: these gases are oxygen, nitrogen, carbonic acid, sulphurous acid, hydrosulphuric acid, ammonia, and occasionally carbonic oxide and light carburetted hydrogen. Generally speaking, the different gases, when pure, are readily distinguished from each other by some well-marked physical or chemical property. The few gases which are coloured are at once indicated by the peculiarity of their tint, conjoined with their characteristic odour: in this manner peroxide of nitrogen, chlorine, hypochlorous acid, chlorous acid, peroxide of chlorine, and bromine vapour are at once recognised.

Many gases have a peculiar and characteristic odour. Some of the most important, however, including oxygen, nitrogen, hydrogen, carbonic acid, carbonic oxide, light carburetted hydrogen, olefiant gas, and protoxide of nitrogen possess little or no odour, and require other means for discriminating them from each other.

(418) In order to aid the operator in distinguishing the different gases from each other, Thénard divided them into four groups, the arrangement being dependent upon the action of a solution of potash upon them, conjoined with the occurrence or the absence of combustion on the application of a lighted match to the gas. The action of potash is ascertained by admitting a few drops of a solution of potash into a test tube filled with the gas, and standing over mercury; on agitating the contents of the tube, it is immediately obvious whether any absorption occurs. The application

* Methyl, ethyl, and trityl, with their hydrides, as well as tritylene, are occasionally present in coal gas, but they will not here be specially noticed, as these hydrocarbons cannot be distinguished from each other except by analysis.

of a lighted match to another small tube filled with the gas shows whether it be inflammable, or whether it extinguishes or supports combustion.

The four groups of gases which are formed by the application of these tests are the following:—

1. Gases which are absorbable by potash, but which are not inflammable.
2. Gases absorbable by potash, but which are inflammable.
3. Gases not absorbable by potash, and not inflammable.
4. Gases not absorbable by potash, which are inflammable.

We proceed to point out briefly the characters of the components of each group.

(419) 1. *Gases which are absorbable by Potash, but are not inflammable*; these are 15 in number:—viz.

1. Hydrochloric acid	9. Nitrous acid
2. Hydrobromic acid	10. Peroxide of chlorine
3. Hydriodic acid	11. Chlorous acid
4. Fluoride of silicon	12. Hypochlorous acid
5. Fluoride of boron	13. Chlorine
6. Chloride of boron	14. Carbonic acid
7. Chlorocarbonic acid	15. Chloride of cyanogen.
8. Sulphurous acid	

Of these gases each of the first eleven reddens litmus paper, when moistened and plunged into it. Hypochlorous acid and chlorine destroy its colour, and bleach it entirely. Carbonic acid is nearly without action, and chloride of cyanogen produces no effect upon its colour. The first six gases fume strongly when mixed with the air, owing to their action on the moisture which it contains: the solutions in water of hydrochloric, hydrobromic, and hydriodic acids are immediately distinguished by the usual tests for them. Each gas also presents certain peculiarities—viz., 1. A small quantity of chlorine produces no change in the hydrochloric gas; 2. In hydrobromic gas it occasions the separation of red fumes of bromine; and 3. In the hydriodic gas violet fumes of iodine appear. 4. Fluoride of silicon is recognised by the gelatinous deposit of silica which water produces when the gas is dissolved in this liquid. 5. The fluoride of boron produces a gelatinous precipitate in a solution of potash, but not in pure water. 6. Chloride of boron is decomposed by water into hydrochloric and boracic acids, which may be recognised in the solution by the appropriate tests. 7. Chlorocarbonic acid has a peculiar, pungent odour, and is decomposed by water into hydrochloric and carbonic

acids. 8. Sulphurous acid is immediately recognised by the suffocating odour of a sulphur match: it is absorbed by the peroxide of lead, and a white sulphate of lead is formed. 9. Nitrous acid is sufficiently characterized by its colour and peculiar odour; and, 10, the same may be remarked of peroxide of chlorine. 11. Chlorous acid has a greener tinge than the peroxide of chlorine, and it yields a bright yellow solution when dissolved in water. 12. Hypochlorous acid has the odour of the bleaching compounds of chlorine with the alkalies and earths, and it rapidly destroys vegetable colours: these three oxides of chlorine detonate by the application of a temperature below that of boiling water. 13. Chlorine is distinguished by its green colour and remarkable odour, by its bleaching action on vegetable colours, and by its sparing solubility in water, which takes up about twice its bulk of the gas. 14. Carbonic acid extinguishes flame, renders lime-water turbid, and is soluble in about its own bulk of water. 15. Chloride of cyanogen is recognised by its pungent odour, and its peculiar irritating effect on the eyes.

(420) 2. *Gases absorbable by Potash and inflammable;* these are only 4 in number:—viz.,

1. Sulphuretted hydrogen	3. Telluretted hydrogen
2. Seleniuretted hydrogen	4. Cyanogen.

These gases are recognised with great facility. 1. Sulphuretted hydrogen has a peculiar odour of putrid eggs; it burns with a blue flame, often attended with a deposit of sulphur: it blackens paper soaked in a solution of acetate of lead, and is decomposed by moist chlorine, with separation of sulphur; water dissolves about twice its bulk of the gas. 2. Seleniuretted hydrogen has an odour analogous to that of the preceding gas; its aqueous solution gradually deposits selenium in the form of a red amorphous precipitate: it precipitates salts of zinc of a flesh-red colour. 3. Telluretted hydrogen is also decomposed by chlorine, tellurium being set free, and subsiding as a brown powder. 4. Cyanogen burns with a rose-edged purple flame; it has a penetrating characteristic odour. If mixed with an equal volume of oxygen, and a red-hot platinum wire be suspended in the mixture, red nitrous fumes are produced by the oxidation of the nitrogen contained in the gas.

(421) 3. *Gases not absorbable by Potash, and not inflammable;* of these also there are four—viz.,

1. Oxygen	3. Nitrogen
2. Protoxide of nitrogen	4. Deutoxide of nitrogen.

1. Oxygen is at once distinguished from all other gases by its

property of kindling a glowing match, by its power of producing red fumes when mixed with deutoxide of nitrogen, and by its insolubility in water when agitated with it. It is absorbed by moistened phosphorus; by a solution of suboxide of copper in ammonia, rendering the colourless solution deep blue; and by a solution of pyrogallic acid in potash, the mixture becoming of an intense bistre colour. Solutions of the sulphides of the alkaline metals also absorb oxygen rapidly. 2. Protoxide of nitrogen, though it rekindles a glowing match, is dissolved when agitated with water. 3. Nitrogen extinguishes the flame of burning bodies; it is insoluble in water, and does not render lime-water turbid. 4. Deutoxide of nitrogen is instantly recognised by the red fumes which it occasions when mixed with air or free oxygen; it is immediately absorbed by a solution of protosulphate of iron, giving the liquid a deep brown colour.

(422) 4. *Gases not absorbable by Potash, which are inflammable;* these gases are 7 in number:—viz.,

1. Hydrogen	5. Phosphuretted hydrogen
2. Light carburetted hydrogen	6. Arseniuretted hydrogen
3. Olefiant gas	7. Carbonic oxide.
4. Oil gas	

1. Hydrogen is inodorous, if pure; it burns with a feebly luminous flame, and if mixed with half its volume of oxygen produces water either by the transmission of an electric spark, or by the action of a ball of spongy platinum. 2. Light carburetted hydrogen burns with a yellowish flame; it is not acted upon if mixed with chlorine over water and screened from light, and is not dissolved by fuming sulphuric acid. 3. Olefiant gas, when mixed with an equal volume of chlorine, even in the dark becomes condensed to an oily liquid which is insoluble in water; it is also absorbed by perchloride of antimony, and by the Nordhausen sulphuric acid: it burns with a brilliant smoky flame. 4. Oil gas is soluble in oil of vitriol, and in alcohol; it burns with a brilliant smoky flame. When the last two gases are mixed together, there is considerable difficulty in identifying the existence of each in such a mixture, and a still greater difficulty occurs when methyl, ethyl, trityl, or their hydrides are present. 5. Phosphuretted hydrogen is distinguished by its peculiar alliaceous odour: it burns with a luminous flame, producing white fumes of phosphoric acid; solutions of the salts of copper, silver, and mercury dissolve it and form brown precipitates. 6. Arseniuretted hydrogen is decomposed if passed through glass tubes heated nearly to redness, a ring of metallic arsenic

being deposited: it burns with a peculiar whitish flame, and deposits a brown stain of metallic arsenic on cold bodies introduced into the burning jet. It is extremely poisonous, and has a peculiar odour of garlic. It may be distinguished from antimoniuretted hydrogen by methods to be described hereafter (709). 7. Carbonic oxide burns with a pale blue flame, producing carbonic acid: it is insoluble in water, and is dissolved by a solution of subchloride of copper in hydrochloric acid.

(423) *General Principles of the Analysis of a Mixture of Gases.*—In a mixture of gases a qualitative examination must be made as a preliminary step in order to ascertain what gases are present. It is of course needless to search for those which mutually condense or decompose each other. Thus ammonia would not be found in a mixture which contained hydrochloric, hydriodic, hydrobromic, sulphurous, or nitrous acid gases. Oxygen would not occur in a mixture in which binoxide of nitrogen was present. Neither could free chlorine or its oxides co-exist with hydriodic or hydrobromic acid, or with olefiant gas, or with the compounds of hydrogen with sulphur, selenium, tellurium, phosphorus, or arsenic: chlorine and its oxides are equally incompatible with ammonia.

The complete analysis of a mixture of different gases is one of the most delicate and difficult branches of chemical analysis, and it is not intended on the present occasion to attempt to give more than an idea of the principles on which such an operation is conducted, and of the apparatus by which it is effected.

As an illustration of the method of proceeding we may take a case of frequent occurrence: viz., the determination of the composition of a sample of coal gas. In this gas, the ingredients which may be present are numerous. These are—1, hydrogen; 2, olefiant gas and other heavy hydrocarbons; 3, light carburetted hydrogen; 4, carbonic oxide; 5, carbonic acid; 6, sulphuretted hydrogen; 7, ammonia; 8, oxygen, and 9, nitrogen, the last two derived from the atmosphere.

A qualitative examination is made thus;—the proportion of ammonia and of sulphuretted hydrogen is usually very minute, and in most cases these gases must be sought for by placing the tests for their presence for some time in a current of the coal gas. In searching for ammonia, a piece of moistened litmus paper, feebly reddened, is placed for a minute in a jet of the issuing gas: if the blue colour be restored, ammonia is present. Paper soaked in a solution of acetate of lead may be subjected to a similar trial: if it turn brown, sulphuretted hydrogen is present. The presence of oxygen is detected by admitting a bubble of the deutoxide of

nitrogen into a tube filled with the gas under trial, and looking through the tube obliquely upon a sheet of white paper; very small traces of oxygen may thus be detected by the red tinge produced, owing to the formation of peroxide of nitrogen. Carbonic acid may be detected by the turbidity which it produces in lime-water or in a solution of subacetate of lead, if thrown up into the gas, whilst standing in a tube over mercury. The existence of the other gases may be assumed, for they are certain to be present, in greater or less quantity. The sulphuretted hydrogen and ammonia are too small in amount to be quantitatively determined; but supposing that oxygen and carbonic acid are found to be present, the proportion of seven different gases will remain to be ascertained. The following method may be adopted for their quantitative determination:—

1. *Carbonic Acid.*—A volume of the gas is confined over mercury, and its bulk is measured, with due attention to temperature and pressure. A piece of caustic potash which has been melted upon the end of a long platinum wire, to serve as a handle, is introduced from below, through the mercury into the tube. After two or three hours the potash is withdrawn; the amount of the absorption indicates the proportion of carbonic acid which was present.

2. *Olefiant Gas and Heavy Hydrocarbons.*—These gases are absorbed by introducing another ball, consisting of porous coke moistened with fuming sulphuric acid. It is necessary, however, before reading off the volume of the gas, to introduce a ball of potash a second time, in order to withdraw the vapour of anhydrous sulphuric acid, which possesses sufficient volatility to introduce a serious error by dilating the bulk of the gas unless it be completely removed. The total amount of absorption will indicate the proportion of olefiant gas, together with the vapours of condensible hydrocarbons.

3. *Oxygen.*—This gas is determined in a similar manner, by employing a ball of moist phosphorus, which must be left in the gas for twenty-four hours; the fresh diminution in bulk, shows the proportion of oxygen.*

* A ball of coke moistened with a concentrated solution of potash and pyrogallic acid may be employed for the same purpose: the absorption in this case is much more rapid.

The use of pellets of appropriate materials may be extended to other gases: for example,

Sulphurous acid may be absorbed by using a ball of moistened peroxide of manganese, or of peroxide of lead; and *hydrochloric acid* is rapidly absorbed by a ball consisting of crystallized rhombic phosphate of soda.

FIG. 304.

4. *Carbonic Oxide.*—The accurate separation of carbonic oxide from the other gases, is not easily effected. The gas may be divided into two portions, one of which is to be carefully measured as it stands over mercury, in the jar, *h*, fig. 304; a small quantity of a solution of subchloride of copper in hydrochloric acid is next added by means of the syringe, *i*, and the mixture is briskly agitated; the gas is then withdrawn by means of the gas pipette shown in fig. 261, p. 54, and transferred by its means to a second graduated tube, also standing over mercury; into this tube a ball of potash on the end of a platinum wire is introduced, for the purpose of absorbing the vapours of hydrochloric acid with which the gas is saturated; its bulk may then be read off, and the volume of carbonic oxide may be known by the loss in bulk which it has experienced.*

5, 6, 7. *Nitrogen, Carburetted Hydrogen, and Hydrogen.*—The determination of the carbonic oxide, however, may be effected along with the carburetted hydrogen and hydrogen without having recourse to absorption. Let a portion of the gas in which the carbonic oxide is still present be now transferred to a siphon eudiometer (fig. 257), and let its bulk, V, be accurately measured; then add about twice its volume of oxygen, and measure the gas a second time: let this bulk be V_1; $V_1 - V$ will give the volume of oxygen which has been added. Let V_2 be the bulk of the gas after the mixture has been exploded by the transmission of the electric spark: $V_1 - V_2$ indicates the diminution in bulk which it has experienced: call this *a*. Then inject a small quantity of a a strong solution of potash, and again note the volume, V_3. The

* The absorption of gases by liquid reagents is much more rapid than when moistened balls are employed, and provided that only very small volumes of liquid are used, the results are equally accurate. Thus, carbonic acid may be absorbed by means of a concentrated solution of caustic potash, one or two drops of which will suffice; and oxygen may be withdrawn by a concentrated mixture of pyrogallic acid and caustic potash.

absorption, $V_2 - V_3$, will be due to the quantity of carbonic acid which has been formed: call this b. The remaining gas, V_3, consists of oxygen in excess, and nitrogen. The quantity of oxygen in excess is ascertained by mixing the residual gas with about twice its bulk of hydrogen, and causing the electric spark to pass a second time. Let the volume of the mixture before firing be V_4, and let V_5 be the bulk after firing: $V_4 - V_5$ will represent the amount of condensation; and one-third of this, or $\frac{V_4 - V_5}{3}$ will be due to the excess of oxygen. On deducting this from the residue, V_3, the difference gives the volume of nitrogen, n; $V_3 - \frac{V_4 - V_5}{3} = n$. The difference between the amount of the oxygen thus found to be in excess, and that originally introduced, will of course represent the quantity of oxygen consumed: call this c: thus $V_1 - V - \frac{V_4 - V_5}{3} = c$.

We have now all the data for calculating the proportions of carburetted hydrogen, of hydrogen, and of carbonic oxide, which are present in the mixture.

Let x represent the quantity of light carburetted hydrogen; this gas requires twice its own volume of oxygen for complete combustion, and furnishes its own volume of carbonic acid, which requires for its formation an equal volume of oxygen, or half the amount consumed; whilst the other half of the oxygen is required by the hydrogen which is condensed in the form of water; $2\,x$ will consequently represent the diminution in bulk of oxygen which occurs on detonation, due to the amount of carburetted hydrogen which is present (401).

Again, when hydrogen is converted into water, it requires half its bulk of oxygen, and both are condensed entirely. If y represent the bulk of the hydrogen, $\frac{3y}{2}$ will be the diminution in bulk of the mixed gases on detonation which is occasioned by the hydrogen in the mixture.

Let z represent the volume of carbonic oxide present; carbonic oxide for its conversion into carbonic acid requires half its bulk of oxygen, the carbonic acid produced occupying the same bulk as the carbonic oxide. $\frac{z}{2}$ will therefore indicate the condensation which occurs on firing the mixture, owing to the carbonic oxide present.

The total condensation in bulk, a, which occurs on firing a mixture of light carburetted hydrogen, hydrogen, and carbonic oxide will consequently admit of being thus represented:—

$$(1) \qquad a = 2\,x + \frac{3\,y}{2} + \frac{z}{2}.$$

Further, the quantity of the carbonic acid, b, formed by the detonation, is composed of a volume of carbonic acid equal in bulk to the light carburetted hydrogen, and a volume equal to that of the carbonic oxide, so that the total quantity of carbonic acid may be thus indicated :—

$$(2) \qquad b = x + z.$$

And lastly, the oxygen consumed, c, will be composed of the following quantities: by light carburetted hydrogen, twice its bulk, $2\,x$; by hydrogen, half its bulk, $\frac{y}{2}$; and by carbonic oxide half its bulk, $\frac{z}{2}$; or the total quantity of oxygen consumed will be the following :—

$$(3) \qquad c = 2\,x + \frac{y}{2} + \frac{z}{2}.$$

From these three equations the values of x, y, z, are determined :—

$$x = c - \frac{a+b}{3};$$
$$y = a - c;$$
$$z = \frac{a+4\,b}{3} - c.$$

Minute directions for the analysis of various gaseous mixtures are given by Regnault, in the fourth volume of his *Cours Elémentaire de Chimie,* which contains a description of a form of eudiometer well adapted for accurate experiments: this eudiometer has been advantageously modified by Frankland and Ward (*Q. J. Chem. Soc.*, vi. 197). Bunsen has also introduced very important improvements in the manipulation and apparatus required for the analysis of gases, which are fully detailed in his *Gasometry,* translated by Roscoe (*see* also the article on Eudiometry, in Liebig and Poggendorff's *Handwörterbuch der Chemie,* vol. ii.); and the modes of manipulation have been still further simplified by Williamson and Russell.

CHAPTER X.

THE METALS.

§ I. General Properties of the Metals.

(424) *General Characters of the Metals.*—The metals, as a class, are characterized by a peculiar lustre termed the metallic lustre. They are possessed of a high degree of opacity, and are good conductors both of heat and electricity. Some of them are also endowed with the properties of ductility, or fitness for drawing into wire, and of malleability, or extensibility under the hammer. Most of them have a high specific gravity. When separated from their compounds by electrolytic action, they appear at the platinode, or negative wire of the voltaic battery.

These properties are not developed equally in all the metals; in some metals one or more of them may be wanting altogether: and there are other substances, not metallic in their nature, in which some of these characters are strongly displayed.

(425) *Lustre, Opacity, and Colour.*—Although, when polished, all metals present the lustre termed metallic, yet most of them may be obtained by minute subdivision in a form devoid of lustre. Iron, copper, platinum, gold, silver, and even mercury may be thus readily procured by processes to be mentioned hereafter.

If, however, these metallic powders be subjected to pressure under the burnisher, a sufficient approximation of their particles is produced to render them capable of reflecting light, and the metallic lustre re-appears. This property admits of being applied in the fine arts: for instance, it is possible to make copies of medals or ancient coins, by employing finely-divided copper, which is introduced with the medal into a mould: by submitting it to pressure, an exact copy of the medal, with a beautifully polished surface, is obtained: the copy is then strongly heated, care being taken to exclude atmospheric air: during the ignition the copy shrinks a little in all directions, but a fac-simile is formed, which is extremely distinct, though reversed, and a little smaller than the original.

Bodies which are not metallic occasionally assume a brilliant surface like the metals. Iodine, which in all its chemical relations is directly opposed to the metals, yet possesses a strong lustre; the

same thing is observable in a form of charcoal, termed by the workmen *kish*, which escape from the vent-holes of the moulds during the process of casting iron. A native form of carbon, graphite or plumbago, has received its popular name of *black-lead* from its metallic appearance.

Metals are among the most opaque bodies with which we are acquainted; but their opacity is not perfect. When reduced to exceedingly fine leaves, a portion of light is transmitted; thus pure gold, of not more than $\frac{1}{800,000}$ inch thick, allows a green light to pass.

The *colour* of the reflected light varies with the nature of the metal. In most cases it is nearly white, with a shade peculiar to each metal: the tints of silver, platinum, tin, cadmium, and palladium, are nearly alike; other metals, such as lead and zinc, have a bluish colour; others, like iron and arsenic, have a greyish hue; calcium and barium are pale yellow; gold is a full yellow; and copper is of a red colour. By repeated reflections from the same metal a distinct colour is often rendered obvious, though it is not seen upon looking at the polished surface. A red tint may thus be made evident in silver, and a violet tinge in steel.

Some of the metals possess a characteristic *odour*: iron, tin, and copper emit, on friction, a smell peculiar to themselves, and arsenic, when volatilized, evolves a powerful odour of garlic. The taste of most of the soluble compounds of the metals is astringent or acrid, and of the peculiar kind termed metallic.

(426) *Hardness, Brittleness, and Tenacity.*—Great differences are observable between the *hardness* of the different metals; steel may be rendered hard enough to scratch glass, while lead will take impressions from the finger-nail, and potassium may be spread like butter. Many of the harder metals are very elastic and sonorous when struck; but these properties are more strikingly displayed in some of the alloys, or compounds of the metals with each other, as in the alloy of tin and copper used for bells, and in the combination of carbon with iron, well known as steel, which, by its high elasticity, is pre-eminently qualified for the construction of the springs used in machinery.

Closely connected with the hardness are the *brittleness* and the *tenacity* of metals, which are very variable. Some, like antimony, arsenic, and bismuth, may be pulverized without difficulty in a mortar, while others, as iron, gold, silver, and copper, require great force to effect their disintegration. The brittleness of some of the metals is materially affected by temperature. Zinc, within the ordinary atmospheric range, is so brittle that it cannot be bent at a

sharp angle without danger of destroying its cohesion, while if heated to between 200° and 300°, it may be wrought with facility. Brass, an alloy of copper and zinc, on the contrary, becomes brittle at temperatures approaching to redness, but while cold it possesses considerable malleability.

Taking the tenacity of lead = 1, the tenacity of the different metals, after annealing, will be represented according to Wertheim's experiments as follows:—

Lead	1	Silver	8·9
Cadmium	1·2	Platinum	13
Tin	1·3	Palladium	15
Gold	5·6	Copper	17
Zinc	8	Iron	26

The tenacity of the metals has been measured by fixing firmly in a vice one end of a bar or wire of the metal, the strength of which is to be ascertained, and attaching to the other end a convenient support for weights which are cautiously increased until the wire breaks. By comparing together the weights required to determine the rupture of the different metals for bars of equal section, a comparative table of tenacity may be formed. Various circumstances materially influence the strength of the same metal;* such as its purity, the mode in which the bar has been prepared (whether by casting, by forging, or by wire-drawing), the temperature at which the comparisons are made, the application or omission of the process of annealing, and the manner in which the tension has been exerted, whether gradually or suddenly. Different observers, in consequence of operating differently in some one or other of these respects, have obtained results which vary from each other considerably. The necessity of attention to these points will be evident on examining the results obtained by Wertheim (*Ann. de Chimie*, III. xxii. p. 440), who has given an elaborate series of experiments upon the tenacity of different metals, the most important of which are embodied in the following table. The numbers represent the weight in kilogrammes which a bar of each metal of 1 millimetre square would support without breaking, both when the strain is gradually increased and when suddenly applied:—

* Deville, for example, by melting cobalt in a crucible of lime, has obtained it free from carbon and other impurities, in the form of a ductile mass of such tenacity as to furnish a wire capable of supporting twice as great a weight as a wire of pure iron of similar dimensions; and a wire of nickel prepared in a similar way, though inferior in tenacity to one of cobalt, surpasses one of iron in the ratio of 3 to 2.

	60° F.		212° F.	392° F.
	Gradual.	Sudden.		
Cast steel, drawn		83·8		
Do. do., annealed . . .	65·7			
Piano wire, (steel)	70·0	99·1		
Do., annealed	40·0	53·9	59·10	50·90
Iron wire	61·10	65·1		
Do., annealed	46·88	50·25	51·10	46·9
Copper wire	40·30	41·0		
Do., annealed	30·54	31·68	22·10	
Platinum wire	34·10	35·0		
Do., annealed	23·50	27·70	22·60	19·70
Palladium wire		27·2		
Do., annealed	27·4			
Silver wire	29·0	29·6		
Do., annealed	16·02	16·5	14·00	14·00
Zinc, commercial, drawn . .	12·80	15·77		
Do. do., annealed . . .		14·40	12·20	7·27
Pure Zinc, cast	4·5			
Gold, drawn	27·0	28·4		
Do., annealed	10·08	11·1	12·60	12·06
Cadmium, drawn	2·24			
Do., annealed		4·81	2·60	
Lead, cast	1·25	2·21		
Do., drawn	2·07	2·36		
Do., annealed	1·80	2·04	0·54	
Tin, drawn	2·45	3·0		
Do. do., annealed . . .	1·70	3·62	0·85	

It will be seen, from an inspection of this table, that the general effect of heat is to diminish the tenacity of the metals, except in the case of iron, steel, and gold, the tenacity of which seems to be somewhat increased by a heat of 212°; this is particularly so with iron: by a further elevation of temperature the tenacity is again diminished. The influence of annealing, or heating the bar to dull redness, and allowing it to cool slowly, is still more remarkable, for by this means the tenacity of gold is reduced more than half, that of silver nearly as much, that of platinum about one-third, and that of iron and copper about a fourth.

(427) *Malleability and Ductility.*—The following metals are termed malleable metals, *i. e.* metals which may be reduced to thin leaves either by lamination between rollers, or by hammering:—

Gold	Palladium	Lead
Silver	Iron	Cadmium
Copper	Aluminum	Nickel
Platinum	Tin	Cobalt.
	Zinc	

Lithium, potassium, and sodium, as well as mercury when in a frozen state, likewise admit of extension under the hammer. Gold far surpasses all the other metals in malleability, being capable of reduction into leaves so thin that a square foot weighs less than 3 grains, and the film does not exceed the 200,000th of an inch in thickness. Silver and copper may also be reduced to leaves of great tenuity. The other metals may be rolled into foil, but cannot be hammered into leaf. At the Industrial Exhibition of Breslau, 1852, an album of leaf iron was exhibited, the sheets of which did not exceed the $\frac{1}{2500}$th of an inch in thickness, and a square inch of the leaf weighed only three-fourths of a grain. Nickel and cobalt are far less malleable than the other metals in the list. The metals become denser in rolling, and are often rendered so hard by the operation that they require to be annealed between every second or third rolling. During the processes of hammering and rolling, much heat is extricated.

The metals may be arranged in the following order of ductility, the property being possessed to a nearly equal extent by the first five upon the list:—

Gold	Palladium	Zinc
Silver	Cadmium	Tin
Platinum	Cobalt	Lead
Iron	Nickel	Magnesium
Copper	Aluminum	Lithium.

Ductility is peculiarly displayed by the first 7 metals on the list. Wollaston procured a wire of platinum, the diameter of which did not exceed the $\frac{1}{30,000}$th of an inch, by placing a wire of platinum in the axis of a small cylinder of silver, and reducing the compound wire to the utmost practicable tenuity in the ordinary way, by drawing it through holes made in a hard steel plate, termed a draw-plate; the apertures through which the wire was made to pass diminishing in size by regular gradation. Both metals were thus attenuated, *pari passu*, and the silver was finally dissolved off by nitric acid, which left the platinum unacted upon. Gold wire equally fine was obtained by a similar process (*Phil. Trans.*, 1813). Steel wires of extreme fineness have been produced in a similar manner, the silver being, in this case, dissolved by the action of mercury. Zinc, tin, lead, magnesium, and even lithium, may also be obtained in the form of wire, but with difficulty, on account of their feeble tenacity.

The malleability of a metal is by no means always proportioned to its ductility: iron, though it may be reduced to wires of ex-

treme fineness, is not nearly so malleable as gold, silver, copper, and some other metals which are inferior to it in ductility. A few substances which are not metallic exhibit, when in a state of semifusion, a very perfect ductility. Half-melted glass shows this property in a marked degree; it may be spun into very fine threads, which have even been woven into a species of cloth, designed for ornamental purposes.

It is obvious that the properties of brittleness, tenacity, ductility, and malleability, must be materially dependent upon the texture of the metal. This is strikingly exemplified in the variation in tenacity exhibited by the same metal under different circumstances. Silver, in ordinary cases, is tough, ductile, and malleable; by repeated heatings and coolings, however, its particles arrange themselves in a crystalline manner, and it then becomes very brittle. Copper, when deposited in crystals by slow voltaic action, is very hard and brittle; but when the action is more rapid it is soft and tough, and the metal then exhibits a fibrous character: and it may be stated, as a general principle, that the crystalline metals, such as zinc, antimony, bismuth, and arsenic, are the most brittle; while those which, like iron, have a fibrous structure, are possessed of a high degree of tenacity.

The structure of a metal is easily displayed in many cases, by placing it in solvents the operation of which is very gradual. Some of the metals which fuse readily may be obtained in crystals without difficulty, by allowing a few pounds of the melted metal to cool slowly, and pouring out the interior portions before the whole has had time to solidify; the inner walls of the cavity are then found to be lined with crystals. Bismuth is particularly well adapted to this process. The less fusible metals, such as copper, iron, and silver, may often be crystallized from their solutions by slow voltaic actions. Many of them—as, for example, gold, silver, and copper—occur native in crystals. A large proportion of the metals crystallize in forms belonging to the regular system.

(428) *Specific Gravity.*—Wide differences are observable in the specific gravity of the metals. In the annexed table, variations are exhibited between the extremes of iridium and platinum, the heaviest known forms of matter, on the one hand, and lithium on the other, which has little more than half the density of water. The lighter metals are all characterized by their powerful affinity for oxygen; those which are least oxidizable possessing generally the highest specific gravity. In a few instances, the most marked of which is platinum, the density may be somewhat increased by rolling and hammering; but this is not usually the case.

Specific Gravity of the Metals.

Metal.	Sp. Gr.	Observer.
Platinum	21·5	Wollaston.
Osmium.	21·4	Deville and Debray.
Gold	19·34	G. Rose.
Uranium	18·4	Péligot.
Tungsten	17·6	D'Elhuyart.
Mercury	13·596	Regnault.
Palladium	11·8	Wollaston.
Ruthenium	11·4	Deville and Debray.
Lead	11·36	Reich.
Silver	10·53	G. Rose.
Bismuth	9·799	Marchand and Scheerer.
Cobalt	8·95	Rammelsberg.
Copper	8·92	Marchand and Scheerer.
Nickel	8·82	Tupputi.
Molybdenum	8·62	Bucholz.
Cadmium	8·604	Stromeyer.
Manganese	8·013	John.
Iron	7·844	Broling.
Tin	7·292	Kupffer.
Zinc	7·146	Wertheim.
Chromium	6·81	Wöhler.
Antimony	6·71	Marchand and Scheerer.
Tellurium	6·25	Berzelius.
Arsenic	5·969–5·7	Guibourt.
Aluminum, rolled	2·67	Deville.
„ cast	2·56	Deville.
Strontium	2·54	Bunsen.
Glucinum	2·1	Debray.
Magnesium	1·743	Bunsen.
Calcium	1·578	Bunsen.
Sodium	0·972	Gay-Lussac and Thénard.
Potassium	0·865	Gay-Lussac and Thénard.
Lithium	0·593	Bunsen.

(429) *Fusibility.*—The melting points of the different metals differ not less widely than their densities. Mercury, for instance, remains fluid as low as 39° —F.; potassium and sodium melt below the heat of boiling water. Tin, cadmium, bismuth, lead, zinc, and antimony melt below redness, calcium and aluminum above a red heat. Silver, copper, and gold require a bright cherry-red heat; iron, nickel, and cobalt a white heat; while platinum, iridium, rhodium, and several others, require the intense heat of the voltaic battery, or of the oxyhydrogen blowpipe, to effect their fusion.

Order of Fusibility of the Metals.

	°F.	°C.	
Mercury	—39	—39·4	Hutchins.
Potassium	136	58	Gay-Lussac and Thénard.
Sodium	207·7	97·6	Regnault.
Lithium	356	180	Bunsen.
Tin	442	228	Crichton.
Cadmium	442	228	Stromeyer.
Bismuth	507	264	Rudberg.
Lead	617	325	Rudberg.

	°F.	°C.	
Tellurium . . . Arsenic	undetermined.		
Zinc	773 . .	412 . .	Daniell.
Antimony . . .	a little below redness.		
Calcium . . . Aluminum . . .	above a red heat.		
Silver	1873 . .	1023 . .	Daniell.
Copper	1996 . .	1091 . .	Daniell.
Gold	2016 . .	1102 . .	Daniell.
Cast iron . . .	2786 . .	1530 . .	Daniell.
Cobalt . . . . Nickel . . . . Wrought iron . . Manganese . .	highest heat of forge.		
Molybdenum . . Tungsten . . . Chromium . . . Palladium . . .	agglomerate, but do not fuse in the forge.		
Platinum . . . Rhodium . . . Iridium . . . . Vanadium . . .	require the heat of the oxyhydrogen blowpipe.		

Some metals near their melting points, before undergoing complete fusion, pass through a soft, intermediate stage, in which, if two clean surfaces be presented to each other, and strong pressure or hammering be employed, they unite, or weld together, so as to form one continuous mass. Iron, lithium, and potassium afford the most striking instances of this. Palladium is also, in a minor degree, susceptible of it.

(430) *Volatility.*—Many of the metals admit of being volatilized without difficulty. Mercury, when heated under ordinary atmospheric pressure, boils, and is reduced to a perfectly colourless, transparent vapour, at about 662°. It is important to observe that this dry vapour, though metallic, is an insulator of electricity, and will allow the transmission of distinct electric sparks as readily as atmospheric air. The insulating power of mercurial vapour, on the one hand, and the small specific gravity of potassium, of sodium, and of lithium, on the other, show that there is nothing inconsistent with facts in the supposition that hydrogen itself, although the lightest known form of matter, and though gaseous, and consequently an insulator of electricity, may possibly be a metal; and indeed, in its chemical properties, it approximates very closely to this class of bodies. Seven of the metals are sufficiently volatile to be distilled from the compounds from which they are obtained—viz.,

Mercury	Zinc	Potassium
Arsenic	Cadmium	Sodium.
Tellurium		

Arsenic is volatilized below redness, and even before it has assumed

the liquid form: cadmium requires a full red heat, and zinc, potassium, and sodium a higher temperature. Those metals which are generally considered fixed in the fire are likewise volatilizable to a certain extent. In the process of lead smelting, one-seventh of the lead escapes up the chimney, and would be wasted unless means for collecting it were adopted. Even copper is not absolutely fixed in the fire. My friend, Dr. Percy, some years ago, showed me a remarkable illustration of this fact: he has in his possession part of a beam which, for many years, was suspended over a furnace in a copper-smelting house in Norway; the whole beam, of which this is a fragment, contains minute beads of metallic copper studded through its texture: the copper must have been raised in vapour and so deposited within its fibres. Gold has been found similarly studding the beams of refineries; and it may be seen to undergo volatilization in the focus of an intensely powerful burning glass. Fine wires of the most refractory metals may be dispersed in vapour by transmitting the discharge of a powerful Leyden battery through them.

(431) *Conducting Power for Heat and Electricity.*—The great differences of expansion exhibited by different metals when exposed to equal degrees of temperature, have already been pointed out (126); and it may be stated generally that each metal possesses a specific expansion: the conducting power of each metal, both for heat (143), and for electricity is also definite (209 *a*, 242); in general it is found that the best conductors of heat are also the best conductors of electricity: but though conductors in the solid and liquid conditions, the metals are insulators in the aëriform state.

(432) ALLOYS.—Metals enter into combination with each other, and form compounds termed *alloys*, many of which are most extensively used in the arts. Comparatively few of the metals possess qualities such as render them suitable to be employed alone by the manufacturer; zinc, iron, tin, copper, lead, mercury, silver, gold, and platinum, constitute the entire number so used. Arsenic, antimony, and bismuth, are too brittle to be used alone, but are employed for hardening other metals. Many of the physical properties of these metals are greatly altered by combination with others; the combination or alloy being often adapted to purposes for which either metal separately would be unfit. Copper alone is not fit for castings, and it is too tough to be conveniently wrought in the lathe or by the file; but when alloyed with zinc, it forms a much harder compound, which can be cast, rolled, or turned, and which constitutes the different kinds of brass, the qualities of which can be varied by varying the proportions of the two metals.

The addition of nickel to brass destroys its yellow colour, and produces the white compound metal known under the name of German silver. Copper and tin in various proportions yield the hard, tough, but moderately fusible compounds known as bronze and bell metal. When the metals combine with mercury, the resulting body is called an *amalgam*.

In most cases these compounds of metals with each other are united by weak affinities; for it appears necessary, in order to produce energetic union between any two bodies, that the substances when separate should exhibit great dissimilarity in properties. It has sometimes been questioned whether alloys are true chemical compounds: definite compounds of the metals with each other do, however, certainly exist, and some have been found combined in definite proportions in the native state. Such is the case with silver and mercury, which occur crystallized together in the proportion of 1 equivalent of silver to 2 equivalents of mercury ($AgHg_2$): and that the alloys are undoubtedly in many instances true chemical compounds, is further shown by the increase or diminution in density which attends the act of combination; the specific gravity of the alloy being generally either above or below that of the two metals employed. The fusing point of an alloy is generally much lower than the mean of those of the metals which compose it. This circumstance, as well as the alteration which alloys exhibit in their general relations to heat and electricity, are also further evidences of the definite character of these compounds. A remarkable illustration of the influence which the chemical union of the metals exerts upon their fusing point, is afforded by the alloy called 'fusible metal,' which is a mixture of bismuth, of lead, and of tin, in the proportions represented by the formula (Bi,Pb,Sn): they form a compound which melts at 212°, a temperature more than 200° below the fusing point of tin, the most fusible of these metals, and 400° below that of lead. Most frequently, however, the alloys are mixtures of definite compounds with an excess of one or other metal, and the separation of their components from each other is generally easily effected by simple means. Thus by exposing brass to a high temperature, the zinc is volatilized, leaving the copper behind; and from the alloy of arsenic and platinum, a heat sufficiently long continued will expel almost the whole of the arsenic. Even mere mechanical means will sometimes suffice to effect the separation. When silver, for example, is amalgamated with mercury, the amalgam formed is dissolved by an excess of mercury: this excess, however, may be almost entirely removed

queezing the mass through chamois leather; the amalgam is ained in the solid form, while the superfluous mercury, nearly ed from silver, escapes through the pores of the leather.

The chemical properties of an alloy are generally such as night have been anticipated from those of its components. In many instances, however, the alloy of two oxidizable metals is much more readily oxidized than either of its constituents. An alloy of 1 part of lead and 3 parts of tin, for example, burns when heated to dull redness much more easily than its components, and becomes converted into a white ash, used in the preparation of enamels (502). Sometimes an alloy is completely soluble in an acid which is without action upon one of its components:—German silver, which is a combination of copper with zinc and nickel, is readily dissolved by diluted sulphuric acid, though the acid will not attack metallic copper; and in a similar manner, an alloy of platinum with ten or twelve times its weight of silver is entirely dissolved by nitric acid, although platinum alone resists the action of the acid completely.

The ductility of metals is usually impaired by combination with one another. Alloys of two brittle metals are invariably brittle: such is the case with the compound of arsenic and bismuth. Alloys of a brittle with a malleable metal are also brittle. Even when two malleable metals are united, the compound is sometimes brittle; gold, for example, when alloyed with a minute portion of lead, splits under the hammer. Generally speaking, the hardness of metals is increased by alloying them; of this a familiar instance is afforded by the standard coin of the realm: both gold and silver, when unalloyed, are not sufficiently hard to resist attrition to the degree required for the currency, but the addition of $\frac{1}{10}$th or $\frac{1}{12}$th of their weight of copper to either metal increases its hardness to the requisite extent.

The more important alloys will, however, be best considere separately, when the individual metals which enter into their cor position are described.

(433) *Condition in which the Metals occur in Nature.*—ties which unite the components of an alloy are feeble, and easily severed; but the compounds formed by the metals wit class of substances known as non-metallic, are for the mos held together by affinities of a very powerful order, and compounds are in a chemical point of view much more int important than the alloys. With some of the metals ombine in small proportion without app aracter; and, in fact, these c

more resemble alloys than any other class of combinations: the most remarkable instances of carbides and silicides are furnished by iron, which, in its modifications of steel and cast iron, is combined with variable quantities of these elements. Many of the compounds of the metals with sulphur preserve the metallic lustre, as is seen in galena and pyrites, yet lose nearly all the other physical properties by which the metals are recognised; ductility, malleability, and power of conducting electricity are extremely impaired. The metallic character is still more completely destroyed by oxygen, which converts the metals into bodies apparently earthy, as in the familiar cases of lime, magnesia, alumina, and oxide of zinc: whilst chlorine and its allied group of elements form compounds which are most of them soluble, and possess all the qualities of true salts. The energy with which iron, zinc, and many other metals combine with oxygen is very remarkable; and the affinities of chlorine are still more active.

The more common metals, on account of their powerful affinity for oxygen and sulphur, are very rarely met with in the uncombined form. Some of those which are less abundant are however found naturally in the metallic condition: such is the case with gold, silver, mercury, platinum, and copper. They are then said to occur in the *native state*. Many are found alloyed with each other: gold, for instance, forms native alloys with palladium and with silver; silver with mercury; antimony with arsenic. The occurrence of native metals or natural alloys is, however, an exceptional circumstance, for the majority of the metals are found in combination with other elements. Oxygen and sulphur, in particular, from their powerful affinities and the abundance in which they occur, are the bodies most frequently associated with them; at other times arsenic, and more rarely chlorine, are the mineralizing agents. These compounds, whether oxides, sulphides, arsenides, or chlorides, constitute what are termed the *ores* of the metals.

(434) *Distribution of the Metals.*—Next to silica in its various forms, the most abundant components of the rocks and superficial portions of the globe, are the compounds of lime, alumina, and magnesia. These earths are themselves oxides of metallic bodies, the affinity of which for oxygen is so intense that they are never isolated from it except for scientific purposes in the laboratory of the chemist. In their oxidized form they are everywhere scattered in abundance over the face of the globe. It is not so with those metals which man is in the habit of separating from their ores upon the large scale, and of employing for the various requirements of civilized society in the metallic state. Most of the ores of

the highest importance and utility, constitute but a comparatively small portion of the components of the earth's crust; but this deficiency in their relative proportion is more than compensated by the mode of their distribution, for they are not dispersed at random, or diffused in minute quantity uniformly throughout the mass of the earth, but are collected in thin seams or beds, which form *mineral veins*.

Man has hitherto been able to penetrate but to a very small depth into the body of the earth, the deepest excavation which he has been enabled to make being not greater, in proportion to the diameter of the earth, than the thickness of an ordinary sheet of writing paper to a globe of two feet in diameter. Geological observations have shown, and any person who has traversed a railway cutting has had a partial opportunity of convincing himself of the fact, that a great part of the superficial portions of the globe consists of a succession of beds or layers, —*strata*, as they are commonly termed, which rest one above another: these beds in some places retain nearly their original horizontal direction; but usually they have assumed a position more or less inclined, so as to form a considerable angle with the surface. The same stratum is liable to great variations in thickness in different parts, but each bed is found to occur in a uniform position in the series, the successive strata following each other in regular order, the uppermost being those of most recent formation. In this way the London clay rests upon the chalk, the chalk upon what is termed the green-sand, the green-sand upon the gault, and so on. The stratified or *sedimentary* rocks rest upon others, which, like granite, porphyry, and basalt, show no appearance of stratification, but bear marks, more or less evident, of having undergone igneous fusion.

Occasionally it happens that a thin bed of metallic ore forms a part of the regular succession of the strata; thus in Staffordshire, over many square miles of country, thin bands or seams of the ore termed clay iron-stone, varying in thickness from 2 to 8 inches, are found lying between the beds of coal. Usually, however, the metalliferous masses occur in still older formations; such as in the mountain limestone of Cumberland and Derbyshire, or in the granite and clay-slate, as in Cornwall: they are then found in fissures which traverse the ordinary strata of the district, and assume a direction which, though it never becomes quite vertical, still approaches more or less towards this position. These fissures vary in thickness from a few inches to as many feet; they are often filled with masses of basalt, granite, or trachyte (which have

been injected from below, whilst the materials were in the molten state under the effects of subterranean heat), and then constitute what the miner terms *dykes*; but in other cases they are filled with metallic ores, and form mineral veins, or *lodes*. The ore sometimes occurs nearly pure; at others mingled with quartz, fluor-spar, and various crystallized minerals, or else with earthy impurities of different descriptions. These veins extend from the surface downwards, often to a depth greater than can be followed even in the deepest mines. The veins which occur in the same district usually run in two directions, nearly at right angles to each other, the principal or original veins being traversed by the others. In Cornwall, for example, the metalliferous veins run nearly east and west, but they are occasionally intersected more or less obliquely by other lodes, to which the term of *caunter* (contrary) *lodes*, or *cross courses*, has been given.

These cross courses, however, are by no means always metalliferous; they often appear to have been occasioned by the action of a force emanating from below, which, after bending and splitting the original strata, produced the fissures which were subsequently filled with quartz, clay, and various minerals. Such cross courses as these not seldom occasion the miner much trouble and perplexity, since the subterranean force necessary to produce them is often attended with great displacement of the original strata. A valuable vein of ore is from this cause frequently interrupted, and is sometimes lost altogether for want of knowing in what direction to seek for it. This sudden break in a vein, and its displacement, in mining language, is termed a *fault*. It is very rarely that a single mineral vein occurs alone; usually several are found together.

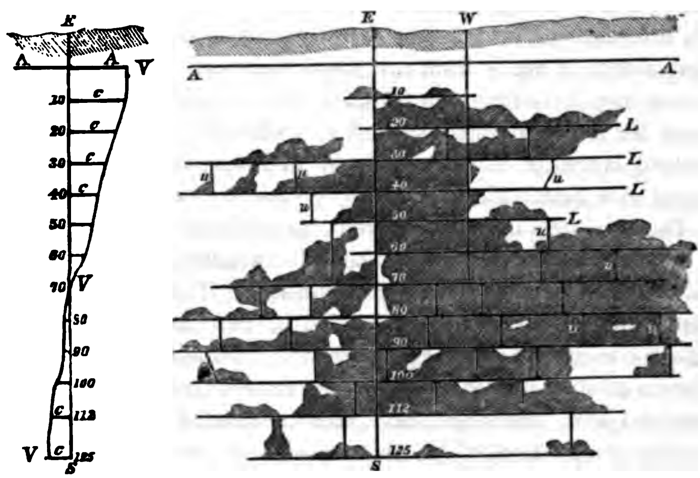
The thickness of the same vein, as might be expected, is subject to great variations; at one time it dwindles to a mere thread, at others it attains considerable expansion. The most productive veins usually occur near the junction of two dissimilar kinds of rock—the metallic ores having probably accumulated there in consequence of slow voltaic actions which have been going on through uncounted ages, and which have been occasioned by differences in chemical composition of the two contiguous rocks: in Cornwall, for example, where so large a proportion of the mineral wealth of Great Britain is accumulated, the most important mines occur upon the junction of the granite with the clay-slate or *killas*.

(435) *Mining Operations.*—The existence of a vein having been ascertained, and its dip and general direction having been determined, the miner commences by sinking a vertical pit, or *shaft*, in such a manner that he calculates upon cutting through

the lode at some 30 or 40 fathoms below the surface. When he has reached the lode, he *drives* a gallery, or *level*, horizontally into it, right and left, raising the ore to the surface through the shaft. If the produce be such as to encourage him to proceed, a second shaft is sunk in the course of the lode, at the distance of about 100 yards from the first, and into this the gallery or level is driven, so as to facilitate the ventilation of the mine and the extraction of the ore. In order to be able to remove the ore from other parts of the lode above and below the point at which the first level is made, the shaft is continued downwards, and other galleries, or *cross cuts*, as they are termed, are made, both above and below the first level, at intervals of ten fathoms, to meet the lode at different points; these cross cuts are at right angles to the levels. Fig. 305 shows a vertical cross section of the lode at the Callington Mine. E S represents the engine shaft, V V the vein or lode, and *c c* the cross cuts. The levels cannot be shown in this view; but whenever a cross cut meets the lode, a level is driven east and west, in the direction of the lode itself.

Fig. 306 shows the arrangement of the levels in the same mine; E S represents the engine shaft, W, a second smaller shaft,

FIG. 305. FIG. 306.



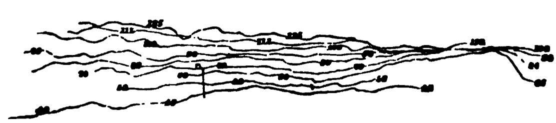


FIG. 307.

and L L L the different levels, the depths of which in fathoms are

indicated by the numbers attached to them; these levels communicate at different points by short cuts, or *winzes*, as the Cornish miners term them; they are shown at *u u*, in various parts, and are needed to facilitate the extraction of the ore from different points of the lode. The different levels are not immediately over, or parallel to each other, but their direction and position varies with that of the inclination and direction of the lode. This is explained by fig. 307, in which the direction of these galleries is exhibited; it represents a *plan* of the mine, supposing the figures to refer to the levels shown in 306: the lode, it will be seen, does not preserve the same dip at all points, being much more nearly vertical at the right than at the left extremity of the plan. The cross cuts cannot be shown in fig. 306. The shaded parts in this figure indicate the portions of the lode which have been already worked away. The galleries in the mine are supported by strong timbering, the object of which is to prevent the rubbish from falling in and overwhelming the men while engaged in their work.

One of the principal difficulties which the miner has to contend with is the continual oozing of water into the mine in all directions. Where the mine, as very often happens, is situated upon the side of a hill, an *adit level*, or watercourse, shown at A A, fig. 306, is carried from the shaft to the lowest accessible point of the surface; and through this the waters of the upper part of the mine readily escape; but when the workings extend below this point, it becomes necessary to pump more or less constantly, and for this purpose powerful steam-engines are required. The galleries and levels are so constructed that the water shall flow from them into the principal shaft of the mine, so that by pumping from the *sump*, or lowest part of this shaft, the whole mine is freed from water. The greater part of the water is lifted only to the adit level, but a considerable quantity is raised to the surface for the purpose of washing the ore.

Much of the excavation is done by hand, with the pickaxe and wedges; but after judicious clearing, gunpowder properly applied facilitates the progress greatly. The quantities of powder used for blasting in the mines are small, usually about two ounces. The process of blasting consists in boring a hole to the depth of 18 inches or 2 feet, somewhat obliquely, under the portion of rock which is to be raised; the powder is then introduced, and the hole is closed by ramming in clay or friable rock. A copper wire runs from the surface down to the charge, and when the ramming or *tamping* is finished, the wire is withdrawn and its place supplied with a pithed rush charged with powder, and the train is fired by

means of a fusee. A safety fusee is now commonly substituted for the copper wire and pithed reed filled with powder. The ore that is detached is raised to the surface of the mine in large wrought-iron buckets, or *kibbles*, which are capable of containing about 3 cwt. of ore.

(436) *Mechanical Treatment of the Ores.*—The extraction of metals from their ores is effected by two classes of operations: those of the first class are mechanical; by their means the earthy parts contained in the matrix or vein-stone are to a certain extent separated: the operations of the second class are chemical, by which the metal itself is procured. The mechanical treatment is influenced not only by the nature and composition of the ore, but also by its market value: an ore of tin, of copper, or of lead, from the higher price which the metal bears, will be worth a more elaborate treatment than an ore of iron or of zinc.

The ores of zinc and of iron are occasionally subjected to the operation of washing; for when they are accompanied by a loose friable clay, the clay admits of being readily diffused in a finely divided state through the water, and is easily removed by its means. The specific gravity of clay is not much more than 2·0, whilst that of carbonate of iron and hydrated oxide of iron varies from 3·8 to 4·0, and that of calamine is about 4·2; consequently particles of these materials of equal size expose a smaller surface in proportion to their weight to the action of water than the clay, and when agitated with water they subside more rapidly; and if subjected to the action of a current of water, they are held for a shorter time in suspension, and are therefore carried by it to a smaller distance.

The same principles apply to the more elaborate processes of washing adopted with the ores of lead and tin. Galena has a specific gravity of 7·6; tinstone of about 7. Sulphate of baryta has a density of 4·6; fluor-spar of 3·1; and quartz of 2·65. When reduced to particles tolerably uniform in size, the earthy portions may therefore to a considerable extent be separated, by the action of water, from the ores of lead and tin.

The following is an outline of the mechanical operations pursued in *dressing* the ores of lead and tin; and the same method is to a certain extent adopted with the copper ores:—

The ore having been brought to the surface, if a lead or copper ore, is first sorted by hand; the purest portions, or *prills*, as the Cornish miners term them, are set aside, and are ready for smelting without further preparation; but the bulk of the ore is broken by hammers into lumps of about the size of a walnut, and the best pieces are again picked out by hand. The rougher portions go to

the crushing mill, which consists of a pair of horizontal cylinders placed parallel to each other at a little distance apart: the cylinders may be either grooved or plain. The ore is supplied to them by a hopper from above. After passing through the mill, the crushed ore is sifted through coarse sieves; the coarser parts are set aside for the stampers, and the finer portion is subjected to the operation of *jigging*. This consists in plunging the ore contained in a sieve into a pit, through which water is constantly flowing: the workman keeps the ore in continual agitation, alternately raising and lowering the sieve, to which he also gives an alternate rotatory motion, taking care always to keep it beneath the surface of the water. By this means the contents of the sieve are separated into layers of different quality. If it be a lead ore which is undergoing treatment, the galena, from its friable character, is easily reduced to small fragments: most of the galena, therefore, passes through the sieve and subsides to the bottom of the pit, whilst what is left upon the sieve consists chiefly of the less friable fluor-spar and quartz. This residue is mixed with the inferior qualities of ore, and is transferred to the stamping mill, whilst the richer part is set aside for smelting.

Tin ore is usually disseminated through a compact hard matrix, and passes at once to the stampers.

The stamping mill consists of five or six upright wooden beams, the lower ends of which are shod with iron, each beam weighing about 2½ cwt. These are placed in a wooden frame, and are alternately lifted up and allowed to fall back upon the ore by the action of arms projecting from a horizontal axle, which is turned by water or steam power. The ore is placed on an inclined plane behind the stampers, and slides down under them, and is crushed. The crushed particles, when reduced to a sufficient degree of fineness, are washed out through a grating in front, by the action of a current of water which is constantly flowing through the mill; the washed ore is carried into a channel in which two pits are formed; in the one nearest the mill the purer and heavier part of the ore, or *crop*, is deposited; whilst the more finely divided portion, technically termed *slime*, or *schlich*, accumulates in the second.

The crushed ore now undergoes a series of washings, the object of which is to separate the impurities from the valuable part of the ore.

The crop is first subjected to washing in the *buddle*; this is a wooden trough, fig. 308, about 8 feet long, 3 wide, and 2 deep, fixed in the ground, with one end somewhat elevated. At the upper end, a small stream of water enters, and is reduced to a uni-

form thin sheet by means of a distributing board, *a*, on which a number of small pieces of wood are fastened to break the stream. The ore to be washed is placed in small quantities at a time upon a board, B, somewhat more inclined than the body of the buddle, and it is spread out in a thin layer; the water carries it forward: the richer portions subside near the head of the trough, and the lighter ones are carried further down. 'The heads' are then tossed in the *kieve*, or tub, shown at *c*, which is filled with water, and ore added by a workman, who keeps the contents of the kieve in continual agitation by turning the paddle or agitator, the handle of which is seen projecting at the top. When the vessel is nearly full, the agitation is stopped, and the kieve is struck smartly upon the side several times, and its contents are allowed to subside; the upper half of the sediment is again passed through the buddle. Various modifications of the washing process are resorted to, but they are all the same in principle.

FIG. 308.

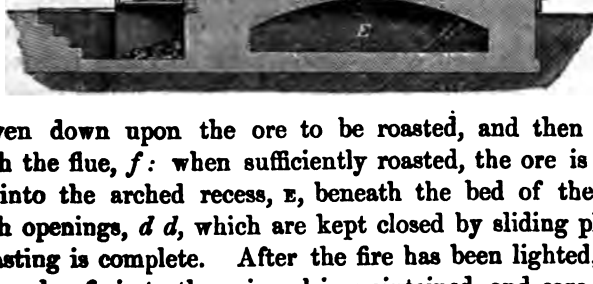
A rough estimate of the value of any sample of dressed ore is obtained by the process called *vanning*:—A small quantity of the ore is placed on a shovel, and agitated gently with a peculiar circular movement in water, then, by giving it a dexterous lateral shake, the different constituents arrange themselves according to their density—the galena, or the tin-stone, at the bottom; above this are iron pyrites and blende; and at the top are the fluor-spar and quartz. The eye then at a glance roughly estimates the quantity of each.

The water employed in the various washings is not allowed at once to run to waste, but is made to pass through a long shallow channel, in which the slime and mud which have been carried away in the different operations may subside. This slime still retains some portion of ore; and in order to recover this as far as possible, it is again subjected to the action of a fine stream of water, either upon an inclined table, which acts in a manner similar to the buddle, or it

is washed upon a swinging table, the bed of which is also inclined, but moveable, and is suspended by chains from supports at the four corners; it is alternately thrust forward two or three inches by the revolution of a cam wheel, and is then allowed to fall back gainst solid wooden bearings with a sudden jar. The ore is spread upon a board which overhangs the upper part of this table, and carried forward by a gentle stream of water; the heavier particles of the ore, owing to the superior momentum which their density gives them, are by this jarring movement of the table carried back to the upper part of it, whilst the lighter impurities are washed away.

(437) *Roasting, or Oxidation.*—The chemical operations are divisible into two main branches, one dependent on the addition, the other on the removal, of oxygen. If the mineral contain volatile ingredients, such as sulphur or arsenic, the process of *roasting*, or oxidation, is first resorted to. In principle it is very simple; the mode of effecting it varies, however, in different cases. In the most common method, a furnace of particular construction, termed a *reverberatory*, is employed. Fig. 309 shows a section of a reverberatory furnace, such as is employed for roasting copper ores; *t* is the platform, from which the hoppers, H H, are charged with the ore, which at proper intervals is allowed to fall upon the bed, *c c*: the fuel is consumed upon a distinct hearth, A, and does not come into contact with the ore, from which it is separated by the bridge, *b*: the heated gases, as they arise from the burning mass, are, from the construction of the arched roof, reverberated,

FIG. 309.



or driven down upon the ore to be roasted, and then pass off through the flue, *f*: when sufficiently roasted, the ore is allowed to fall into the arched recess, E, beneath the bed of the furnace through openings, *d d*, which are kept closed by sliding plates till the roasting is complete. After the fire has been lighted, a constant supply of air to the mineral is maintained, and care is taken

to prevent the heat from rising so high as to melt the ore, which is stirred at intervals to expose fresh surfaces to the action of the air: the sulphur burns off in the shape of sulphurous acid, which escapes into the atmosphere; whilst the arsenic forms arsenious acid, which, though volatile, speedily becomes condensed, and is collected on the sides of the chimney, or else in chambers constructed for its reception, whence it is removed at intervals, and subsequently purified. In metallurgic operations where sulphides of metals of different degrees of oxidability are present, it may happen that the sulphide of the more oxidable metal is completely converted into a metallic oxide, whilst sulphurous acid escapes, and that the sulphide of the less oxidable metal is reduced to the metallic state. Thus in roasting copper pyrites (the mixed sulphides of copper and iron), the iron is wholly converted into oxide, whilst the copper is extracted at once in the metallic state, by a series of careful roastings (733). In the case of sulphide of lead, where the metal possesses but a moderate degree of oxidability, it is also the practice so to regulate the supply of air in the furnace that the sulphur is wholly expelled in the oxidized condition, whilst the greater part of the lead is extracted in the form of metal during a single roasting in the reverberatory (751). Where the metal possesses a high degree of oxidability, as is the case with zinc, it is not practicable to limit the degree of oxidation in this manner during the roasting: the metal itself passes into a state of oxide, simultaneously with the expulsion of the sulphur as sulphurous acid (586).

(438) *Reduction, or Smelting.*—The second chemical process for the extraction of the metals, that of *reduction*, is applicable to most metallic oxides, whether of natural or of artificial origin. The object in this case is to remove the oxygen, by presenting to the mineral some body which, at a high temperature, has a stronger affinity for oxygen than the metal itself possesses. The furnaces employed in this operation are often of great size, and vary in form with the nature of the metal: in them the ore is heated intensely, in contact with carbon; carbonic oxide and carbonic acid are thus produced, and from their gaseous nature are instantly removed from the sphere of action. It becomes necessary at this stage to get rid completely of the earthy and other impurities of the ore, which the mechanical operations never succeed in removing entirely, and which often form a large proportion of the ore. In order to effect this, certain fluxes, or substances which are capable of forming fusible compounds with the earthy matters, are added at the same time with the carbon; these melt and form a

kind of glass, through which the reduced metal, from its superior density, sinks, and is thus completely defended from contact with the air: the metal is at suitable intervals drawn off from the bottom of the furnace, while the melted glass—or *slag*, as it is termed—runs off at an aperture left in the side for the purpose. Limestone is in some cases added to the ore with the view of aiding the fusion of the siliceous impurities: in other instances fluor-spar or some other readily fusible material is added, for the purpose of increasing the fluidity of the slag. Much judgment is required in the selection of the flux, and in deciding upon the proper proportion to be added: frequently this object is economically effected by a judicious mixture of different ores of the same metal, each of which aids the other by supplying some compound which was wanting to render the slag sufficiently fusible.

The various modifications of these processes will be described as they present themselves in connexion with the different metals which require these modifications. Other modes of separating individual metals are employed, which will be alluded to in their respective places. For details upon metallurgic processes, the fourth volume of Dumas' valuable work, *Traité de Chimie appliquée aux Arts*, may be consulted; and the second and third volumes of the same work contain many excellent descriptions of processes in which metallic chemistry is applied to the purposes of industry and commerce. Phillips's *Metallurgy* is a smaller and more compendious treatise on this subject.

(439) *Classification of the Metals.*—The metals may be divided into seven groups (page 10), regard being principally had in this arrangement to the convenience of indicating the method of testing for the presence of the metal, in the ordinary processes of analysis; in consequence of which it is sometimes necessary to depart from the strictly natural order.

In treating of the groups of the non-metallic and electro-negative elements, it has been remarked that the electro-negative character of those belonging to the same group is most strongly marked in those which have the lowest combining number; chlorine, for example, being more active than bromine, and bromine than iodine. With the basylous or electro-positive elements, the reverse generally holds good; the basic power of potassium, for example, being greater than that of sodium, and that of sodium being superior to the basic power of lithium.

I. The metals of the alkalies; these are three in number—viz.,

1. Potassium 2. Sodium 3. Lithium.

These metals present a close analogy in properties; sodium, which is intermediate in properties between potassium and lithium, possessing a combining number which is the arithmetic mean of the two, for $\frac{39+7}{2}=23$. A similar remark is applicable to the intermediate member of some of the other groups.

The corresponding salts formed by the metals of the alkaline group are isomorphous only when they contain equal atomic proportions of water of crystallization. With these metals will be described the salts of oxide of ammonium: they are isomorphous with the salts of potassium, and indeed present the closest analogy with them.

The metals of the alkalies are distinguished by the following characters:—They are soft, easily fusible, and volatile at high temperatures: they have an intense affinity for oxygen, and become tarnished immediately that they are exposed to the air: when thrown upon water, they decompose it at all temperatures with rapid disengagement of hydrogen: they each form two oxides, but only one of these, the protoxide, combines with acids: these basic oxides combine with water with great avidity, and are dissolved by it, forming solutions which are powerfully caustic and alkaline. In these oxides the basic quality, or their capacity for saturating the acids, is developed to the highest degree. The alkalies, when exposed to the air, either in the solid form or in solution, absorb carbonic acid rapidly: each alkali forms with this acid two salts, a carbonate and a bicarbonate, both of which are freely soluble in water. The metals of the alkalies combine with sulphur in several proportions; all of these compounds, also, are soluble. With chlorine they form but a single chloride; but their oxides have the power of combining with chlorine, and forming compounds possessed of bleaching properties. Lithium, from the sparing solubility of its carbonate, forms the connecting link between this group and the one which follows it.

II. The metals of the alkaline earths are four in number—viz.,

1. Barium	3. Calcium
2. Strontium	4. Magnesium.

The first three of these metals decompose water at all temperatures with great rapidity; with the exception of barium, they each form but one oxide, and this oxide is soluble to a certain extent in water, and is capable of combining with acids. They form several sulphides which are soluble in water; the protosulphides being less so than those which contain higher proportions of sulphur. With chlorine their oxides form bleaching compounds. Their carbonates

are insoluble in pure water, but are soluble to a small extent in water charged with carbonic acid. The salts of these metals are in many cases isomorphous. Magnesium—from its power of resisting oxidation at the ordinary temperature of the air, its volatility at high temperatures, the isomorphism of the salts of its oxide with those of oxide of zinc, the sparing solubility of its oxide and its sulphide, the solubility of its sulphate, and several other particulars—stands in closer relation to zinc and cadmium than to the group of the metals of the alkaline earths, with which latter, for convenience, it is usual to associate it. Magnesium, zinc, and cadmium, all burn with flame when heated in air to a sufficiently high temperature, and each of these metals forms but a single salifiable oxide.

III. Metals of the earths; ten in number:—viz.,

1. Aluminum	5. Yttrium	8. Cerium
2. Glucinum	6. Erbium	9. Lanthanum
3. Zirconium	7. Terbium	10. Didymium.
4. Thorinum		

The oxides of this class are insoluble in water; several of them are dissolved by solutions either of the caustic alkalies or of their carbonates. Aluminum and glucinum do not decompose water at ordinary temperatures, unless the metals are in a very finely divided state; the other metals of this group are scarcely known in an isolated form. The basic character of the oxides of this group of metals is much less marked than that of the preceding ones. Many of these metals are very rare, and their properties have been but imperfectly examined. Aluminum, by the isomorphism of its oxide with sesquioxide of iron, the volatility of its chloride, its slight affinity for carbonic acid, and other peculiarities, connects this group with the one which follows.

IV. Metals more or less analogous to iron; eight in number:—viz.,

1. Zinc	4. Nickel	7. Chromium
2. Cadmium	5. Uranium	8. Manganese.
3. Cobalt	6. Iron	

These metals, when heated to dull redness, decompose the vapour of water if it be transmitted over them, and become converted into oxides, whilst hydrogen escapes; they are also soluble with effervescence and evolution of hydrogen in diluted sulphuric or in hydrochloric acid. The protoxides of these metals are powerful bases: these protoxides, with the exception of that of uranium, are dissolved more or less freely by ammonia, especially if chloride of ammonium

be present in the solution. Zinc and cadmium, like magnesium, form only a single oxide, chloride, and sulphide; but each of the other metals forms a sesquioxide, which, excepting in the case of those of cobalt and nickel, combines with acids and forms salts: they also form an oxide of the form MO,M_2O_3 corresponding with the magnetic oxide of iron (FO,Fe_2O_3). Several of the metals of this group—viz., iron, chromium, and manganese—form powerful metallic acids, which are very soluble in water. Hydrated sulphides of these metals are produced by the addition of a solution of sulphide of potassium or of ammonium to a solution of their salts; the precipitate so occasioned is insoluble in excess of the alkaline sulphide. The salts of sesquioxide of chromium, however, are precipitated as oxide of chromium, not as sulphide. Sulphuretted hydrogen gas, when transmitted through the solutions of these metals acidulated with sulphuric acid, occasions no precipitate of sulphide, excepting in the case of the salts of cadmium. Corresponding salts of the protoxides of this group are isomorphous; and the salts of the sesquioxides with the same acid are likewise isomorphous with each other. Chromium and manganese also exhibit an isomorphous relation to the sulphur group, inasmuch as the corresponding sulphates, chromates, and manganates have the same crystalline form. In the case of manganese a singular connexion with the halogens is exhibited in the isomorphism of the permanganates with the corresponding perchlorates and periodates, 2 atoms of manganese being isomorphous with 1 atom of chlorine or of iodine.

V. Metals which yield powerful acids with oxygen; of these there are ten, as follow:—viz.,

1. Tin	5. Molybdenum	8. Arsenic
2. Titanium	6. Tungsten	9. Antimony
3. Columbium	7. Vanadium	10. Bismuth.
4. Tantalum		

A close parallelism in properties exists between tin and titanium, corresponding compounds such as tinstone (SnO_2) and rutile (TiO_2) being isomorphous; they each yield a liquid volatile bichloride, and in this particular, as well as in their powerful affinity for fluorine, they exhibit some analogy with silicon: columbium and tantalum also are similarly related to each other, and to silicon; they both furnish an acid with 2 atoms of oxygen, form a volatile bichloride, and yield definite compounds with fluorine. Molybdenum, vanadium, and tungsten, have also certain analogies with each other, but they are less strongly marked; and the properties

of vanadium are not truly intermediate between those of molybdenum and tungsten.

Protoxide of tin is a powerful base, and this metal forms the transition from the group of the iron metals to the present group. The metals included in this class decompose water when its vapour is driven over them at a red heat (with the exception of arsenic, which is more allied in character to phosphorus than to the metals), but they do not evolve hydrogen when treated with diluted sulphuric acid, owing to the want of basic power in their oxides. Many of them, owing to this tendency to form acids, decompose water with evolution of hydrogen in the presence of a powerful base, such as potash. The metallic acids formed by these metals are, with the exception of arsenic acid, nearly insoluble in water. The persulphides of this group of metals are soluble in the sulphides of the alkaline metals, and in many cases form crystallizable compounds with them.

VI. The next group contains but two metals:—viz.,

1. Copper	2. Lead.

They are not related to each other by any strong chemical resemblances; they exert no decomposing action upon water, even at a full red heat; they form powerful basic oxides, and exhibit a considerable tendency to the formation of subsalts. These metals are not dissolved by either diluted sulphuric or hydrochloric acid; they are precipitated from acid solutions by sulphuretted hydrogen, and their sulphides do not combine with the sulphides of the alkaline metals. Copper forms salts which are isomorphous with those of the protoxides of the metals in the iron group, and in the compounds which it forms with carbonic acid, displays a close correspondence with magnesia, zinc, cobalt, and nickel; and lead in some of its compounds is isomorphous with those of the alkaline earths, but in chemical properties it is more allied to mercury and silver.

VII. The last group consists of the noble metals, of which there are nine—viz.,

1. Mercury	4. Platinum	7. Ruthenium
2. Silver	5. Palladium	8. Osmium
3. Gold	6. Rhodium	9. Iridium.

These metals are unable to decompose water at any temperature. They have but a feeble affinity for oxygen; the oxides of the first five being decomposed below a red heat, the metal remaining in

an uncombined form; and in many cases simple exposure to a strong light produces a similar decomposition: all of them yield more than one oxide capable of forming salts. Mercury and silver are often found mineralized in the form of sulphides, but the other metals of this group usually occur in the native state, several of them being frequently associated together. Their affinity for sulphur and for chlorine is much stronger than for oxygen. All of them form at least two chlorides, and some three or even four: the chlorides of the noble metals have a strong tendency to form double chlorides with the chlorides of the metals of the alkalies.

Silver exhibits considerable analogy with lead; its oxide possesses very strong basic power: palladium is somewhat allied to copper.

§ II. General Properties of the Compounds of the Metals with the non-metallic Elements.

(440) The Oxides.—The most important compounds of the metals with the non-metallic bodies are those which they form with oxygen. The oxides in many cases constitute abundant and valuable metallic ores; such as the different forms of hæmatite, the specular and magnetic iron ores, and tinstone, the ordinary ore of tin.

The metallic oxides may be subdivided into 3 classes:—viz., 1, basic oxides; 2, saline or indifferent oxides; and 3, metallic acids. The compounds of the same metal with oxygen are often numerous; and the extremes, or the oxide with the maximum of oxygen and the oxide with the minimum of oxygen, frequently present chemical qualities of opposite kinds, the former being electro-negative, and possessing acid properties, whilst the lower oxides are electro-positive, or basic, in their nature.

An excellent instance of this kind is afforded in the various oxides of manganese: the protoxide (MnO) is a powerful base, the sesquioxide (Mn_2O_3) is a much weaker base; the red oxide (MnO,Mn_2O_3) is a saline or indifferent oxide, and shows little disposition to enter into combination either with acids or with alkalies, and the same may be said of the black oxide (MnO_2); while the two higher oxides, manganic and permanganic acids (MnO_3 and Mn_2O_7), combine with alkalies, and are true acids. As a general rule, the greater the number of atoms of oxygen which an oxide contains, the less is it disposed to unite with the acids: on the contrary, it frequently possesses acid properties,

and then it unites with bases to form salts. Protoxides generally are strong salifiable bases; they require 1 equivalent of a monobasic acid to form neutral salts. Sesquioxides are weaker bases; their salts are usually unstable; they require 3 atoms or equivalents of a monobasic acid to form a salt which is neutral in composition, though it may not be neutral to test-papers (458); and in general all oxides require as many equivalents of acid as they contain atoms of oxygen in their composition. Some of the metallic acids, like the stannic and titanic, contain 2 atoms of oxygen to 1 atom of metal, but most of them contain 3 atoms of oxygen, such for example as the manganic, ferric, chromic, tungstic, molybdic, and vanadic acids; whilst in a few cases, such as the arsenic, antimonic, and permanganic, the proportion of oxygen is still higher.

The basic oxides in general are devoid of all metallic appearance, and present *par excellence* the characters of earthy matters. The protoxides, when solid, are all insulators of the voltaic current; but some of the higher oxides, such as the binoxide of silver, of lead, and of manganese, allow it to pass with facility. It is singular that all these conducting peroxides may be formed in solutions by the action of the current itself.

The oxides, when found crystallized in the native state, are much harder than the metals that furnish them, and they generally have a specific gravity considerably less than that of the metals themselves. All the oxides are solid at ordinary temperatures; many of them are fusible at a red heat, such, for example, as the protoxides of potassium, of sodium, and of lead, and the sesquioxide of bismuth: but the oxide of copper, molybdic acid, sesquioxide of chromium, and black oxide of iron, require a much higher temperature to effect their fusion. Baryta, strontia, and alumina require the heat of the oxyhydrogen jet; while some oxides, such as lime and yttria, exhibit no appearance of fusion, even after the application of the most intense heat.

As a general rule, the addition of oxygen to a metal renders it much less fusible and volatile. The protoxide of iron, the sesquioxide of chromium, and molybdic acid, are the only oxides which melt at a temperature below that of the metal from which they are produced. A few of the oxides are volatile at moderate temperatures; among these arsenious acid, sesquioxide of antimony, and tessaroxide of osmium. Six only of the basic oxides are soluble in water to any considerable extent—viz., the three alkalies, and baryta, strontia, and lime. The insolubility of the oxides, however, is far from being so complete in general as that of the corresponding sulphides, and consequently, except in particular cases, it is less

advisable in analytical operations to separate the metals in the form of oxides than in that of sulphides.

Those compounds of oxygen with the metals which possess acid characters—such as the chromic, manganic, and arsenic acids—are often freely soluble in water; others, as the molybdic and tungstic acids, are more sparingly taken up; but even those acids which, like the tantalic and telluric, are insoluble, form hydrates which usually redden litmus paper.

Preparation.—Most of the oxides may be procured in combination with water; generally speaking, these hydrated oxides are obtained by double decomposition, on the addition of an alkali to one of their soluble salts: thus sulphate of zinc yields hydrated oxide of the metal on adding hydrate of potash to its solution; $ZnO,SO_3 + KO,HO = KO,SO_3, + ZnO,HO$. The metals which form powerful bases, like those of the alkalies and alkaline earths, retain the water with great obstinacy; while others, which are less powerful bases, such as the hydrated oxide of copper, are decomposed at a temperature below that of boiling water.

The anhydrous oxides may be obtained in several ways:— 1. They may often be formed directly, by burning the metal in air, or in oxygen gas. This process is best adapted to metals which, like zinc or arsenic, are volatile, or which produce fusible oxides, like iron or lead; in such cases the oxide is removed as fast as it is formed, and fresh surfaces of the metal are continually exposed to the action of the gas. Anhydrous potash and soda cannot be obtained by any other method; and it is resorted to on the large scale in the preparation of arsenious acid, and of the oxides of zinc and lead. Several of the metallic protoxides, if roasted at a low red heat in a current of air or of oxygen, absorb an additional quantity of oxygen. Litharge, or protoxide of lead, is thus converted into red lead, $2\ PbO,PbO_2$; and peroxide of barium, BaO_2, may in this way be obtained from baryta. 2. Another method consists in the formation of a nitrate of the oxide of the metal by means of nitric acid; the nitrate is then decomposed by heat, which expels the acid and leaves the oxide: in this way the oxides of mercury, bismuth, antimony, copper, barium, and strontium are prepared. 3. In some cases it is found advantageous to prepare the oxide by the decomposition of the carbonate of the metal by heat. All the carbonates, with the exception of those of soda, potash, and baryta, are decomposed at a red heat. Lime is thus commonly obtained from limestone, which is an impure carbonate. 4. Sometimes the hydrated oxide is first precipitated, as already mentioned, and then rendered anhydrous by heat; in

this manner the sesquioxides of iron and uranium are often prepared. 5. All the acid oxides may be obtained by deflagrating the metal or its sulphide with nitrate of potash; the tendency of the metallic acid to unite with the alkali favours the oxidation of the metal: the higher oxides of osmium, of titanium, of manganese, and of chromium, as well as of some other metals, may be obtained in this way.

Decompositions.—1. By the action of a *red heat* many of the oxides lose their oxygen, either partially or entirely. The oxides of gold, silver, mercury, platinum, and palladium may thus be completely reduced; the peroxides of lead, cobalt, nickel, and barium, return to the state of protoxide; and the metallic acids lose a portion of their oxygen; thus arsenic and chromic acids are converted respectively into arsenious acid and sesquioxide of chromium. It may be stated as a general rule, liable however to exception, especially in the case of the acidifiable metals in the fifth class, that the affinity of a metal for oxygen increases in the inverse proportion of its specific gravity; the lightest metals, such as potassium and sodium, being the most readily oxidized, while platinum, iridium, and gold, which are the densest metals, are also those which show the smallest tendency to combine with oxygen.

2. The oxides are not affected by *hydrogen* gas at the ordinary temperature of the air. All the higher oxides of the metals are readily reduced to protoxides by hydrogen at a low red heat, whilst water is formed; and at a full red heat a large number of them are reduced to the metallic state. This reduction goes on most readily when the current of hydrogen is brisk, so that the vapour of water is carried away as fast as it is formed. The oxides of many of the metals which decompose water at a red heat may nevertheless be deprived of their oxygen in a brisk current of hydrogen; this is the case, for example, with the oxides of iron, zinc, and cadmium. The metals of the alkalies and of the earths are not reducible by hydrogen.

3. The reducing action of *carbon* at a high temperature is still more important; all the metals which yield their oxygen to hydrogen do so to carbon, and potassium and sodium are obtainable from their compounds by its agency. This arises in part from the volatility of these two metals, which is sufficient to enable them to be distilled from the carbonaceous mixture. Lithium and the metals of the earths are not sufficiently volatile to pass over in vapour, and though their affinity for oxygen is less intense than that of potassium or of sodium, they cannot be obtained from their oxides by the action of carbon. It depends upon the nature

of the metal, and upon the temperature employed, whether the gas that is formed during the reduction be carbonic oxide or carbonic acid. The more readily oxidizable metals, such as potassium, zinc, and iron, at a high temperature decompose carbonic acid, so that carbonic oxide only is formed when they are reduced; while if the reduction takes place readily, as is the case with copper and lead, carbonic acid is produced.

4. Dry *chlorine* sometimes, even without the application of heat, decomposes the basic metallic oxides, such as the red oxide of mercury, expelling their oxygen, and converting them into chlorides. At an elevated temperature few of them, excepting those of magnesium and of the earths in the third group, resist its action; the oxides of gold and platinum are simply reduced to the metallic state, but chlorides of the metals are formed in other cases.

If the oxides be hydrated and suspended in water, the action of chlorine is quite different; the metals of the first two groups yield bleaching compounds, and by heat are converted into chlorates and chlorides in the manner already explained (321). The oxides of the third group, the earths proper, experience no particular change, but those in the fourth, or ferric group, are converted into a mixture of chloride and hydrated sesquioxide. The sesquioxides of cobalt and of nickel are usually prepared in this manner: thus, $3\,(CoO,HO) + Cl = CoCl + Co_2O_3,\,3\,HO$.

If the liquid be strongly alkaline, the whole of the metal may be converted into sesquioxide; $2\,(CoO,HO) + KO,HO = Co_2O_3,\,3\,HO + KCl$. Then potash in this case parts with its oxygen, which is transferred to the cobalt, whilst the chlorine combines with the potassium. The protoxide of manganese under these circumstances yields the hydrated peroxide, $MnO_2,2\,HO$.

If the metal be capable of forming an acid with 3 atoms be of oxygen, the process of oxidation may even proceed further, and the sesquioxide may, in the presence of a large quantity of potash, become converted into the metallic acid, which combines with a portion of the excess of alkali; thus in the case of sesquioxide of iron, ferrate of potash is produced $Fe_2O_3,\,3\,HO + 5\,(KO,HO) + 3\,Cl = 2\,(KO,FeO_3) + 3\,KCl + 8\,HO$.

5. Most of the oxides are decomposed more or less completely when heated with *sulphur*; the alkalies and alkaline earths are converted into a mixture of sulphate and sulphide, but the metals of the earths, or those of the third group, are unaltered. Most of the other oxides are converted into sulphides, with escape of sulphurous acid. The oxides are more readily decomposed by sulphur if they be previously mixed with carbon.

(441) *Estimation of Oxygen in Metallic Oxides.*—The composition of a metallic oxide may be ascertained, if it be decomposable by hydrogen, by heating the compound in a current of this gas, collecting and weighing the water produced, and determining the amount of reduced metal which a given weight of the oxide has yielded. In other cases their composition is determined synthetically, a given weight of the metal being converted into oxide, either by heating the metal in a current of air, or by converting it into a nitrate, and afterwards expelling the nitric acid by the application of heat, and weighing the quantity of oxide which is left.

(442) SULPHIDES.—The combinations of sulphur with the metals are numerous; they are in many instances of great value, and form important ores. A large number of the native sulphides often exhibit a high metallic lustre, as is shown by the sulphides of iron, of copper, of lead, and of antimony.

Sulphur frequently combines with the same metal in several proportions, and it usually happens that for each oxide a corresponding sulphide may be formed. Sometimes, as in the case of the metals of the alkalies and alkaline earths, the sulphides are more numerous than the oxides: thus two oxides of potassium, sodium, and barium only are known, but there are not fewer than five sulphides of each of these metals.

All the metallic sulphides are solid at ordinary temperatures. Most of them may be fused at a heat a little above redness, and if the air be excluded, the protosulphides undergo no change in composition; but many of the higher sulphides, such as the bisulphide of iron and bisulphide of tin, are decomposed, and give off the second atom of sulphur, whilst a lower sulphide of the metal is left. Tersulphide of arsenic, or orpiment (AsS_3), and sulphide of mercury, or cinnabar (HgS), may be sublimed if excluded from the air; that is to say, they may be converted into vapour, and recondensed in the solid form: indeed, these sulphides are usually purified by this operation.

The sulphides of all the metals are insoluble in water, with the exception of those of potassium, sodium, calcium, strontium, and barium. Sulphide of magnesium, however, is but sparingly soluble.

The sulphides, like the oxides, may be subdivided into basic and acid sulphides, according to the nature of the metal and the number of atoms of sulphur with which each atom of metal is combined. The protosulphides of the alkaline metals afford illustrations of basic

sulphides, and they enter into combination with the higher sulphides of metals which, like antimony and arsenic, form acids with oxygen. Pentasulphide of arsenic, or sulpharsenic acid (AsS_5), in this way combines with sulphide of sodium, and forms a crystalline soluble compound ($3\,NaS,AsS_5+15\,Aq$); and in like manner pentasulphide of antimony, or sulphantimonic acid (SbS_5), forms a soluble compound with sulphide of sodium ($3\,NaS, SbS_5+18\,Aq$), which crystallizes in beautiful transparent tetrahedra. A large number of similar compounds may be formed with the sulphides of other metals, and these compounds are for the most part soluble in water.

In consequence of the tendency to the formation of these double sulphur salts, many of the sulphides which are insoluble in water are dissolved freely by solutions of sulphide of potassium or of sulphide of ammonium; and this circumstance is frequently taken advantage of in the laboratory during the progress of an analysis, for the purpose of separating certain metals the sulphides of which are soluble in solutions of the sulphides of the alkalifiable metals, from others which are not soluble in these compounds. The following sulphides may be dissolved by a solution of hydrosulphate of ammonia, and by a solution of sulphide of potassium:—

Tersulphide of gold . . .	AuS_3	Tersulphide of tungsten . . .	WS_3
Bisulphide of platinum . .	PtS_2	Tersulphide of molybdenum .	MoS_3
Sesquisulphide of rhodium	Ro_2S_3	Quadrisulphide of molybdenum	MoS_4
Tersulphide of arsenic . .	AsS_3	Protosulphide of tin	SnS
Pentasulphide of arsenic .	AsS_5	Bisulphide of tin	SnS_2
Tersulphide of antimony .	SbS_3	Bisulphide of tellurium . . .	TeS_2
Pentasulphide of antimony	SbS_5	Tersulphide of tellurium . .	TeS_3
Bisulphide of vanadium .	VS_2	The sulphides of iridium.	
Tersulphide of vanadium .	VS_3		

The double salts thus obtained are decomposed by the addition of an acid, such as the sulphuric or the hydrochloric, sulphuretted hydrogen being evolved, whilst the sulphide of electro-negative metal is precipitated: for example, $3\,NaS,SbS_5+3\,HCl$ become $3\,NaCl+SbS_5+3\,HS$.

Decompositions.—If free oxygen or atmospheric air be allowed access to the heated sulphides, they are all decomposed; the sulphur becomes oxidized, and passes off as sulphurous acid, whilst the metal in most cases, as occurs with tin, antimony, and molybdenum, remains in combination with oxygen. The sulphides of the metals of the alkalies and of the alkaline earths become converted into sulphates of the base, and the same thing occurs less completely with many of the metals which have a strong affinity for oxygen; the sulphides of iron, of lead, and of copper, are partially converted into sulphates, but by a stronger heat these sul-

phates lose their acid, and the oxide of the metal only is left. The sulphides of the noble metals, when roasted in a current of air, lose their sulphur, which burns off in the form of sulphurous acid, while the pure metal remains behind, though in the case of silver a portion of sulphate of silver is commonly formed.

Many of the hydrated sulphides become oxidized by exposure to the air, and generally are converted into sulphates.

A large number of the sulphides, especially those of the more oxidizable metals, such as those of iron, zinc, and manganese, are dissolved by diluted hydrochloric acid when cold, and still more readily when heated,—a chloride of the metal and hydrosulphuric acid being formed. Others, such as those of nickel, cobalt, and lead, require boiling with the concentrated acid: it is in this way that hydrochloric acid acts upon the tersulphide of antimony; $SbS_3 + 3\,HCl$ becoming $SbCl_3 + 3\,HS$. Sulphuric acid, when diluted, acts in a similar manner upon the sulphides of the more oxidizable metals, though less readily than hydrochloric acid. The sulphides are all decomposed when heated in a current of chlorine gas, chloride of sulphur and chloride of the metal being formed. This property is sometimes made use of in the analysis of ores consisting chiefly of sulphides, or of sulphides and arsenides of the metals; the volatile metallic chlorides are in this way separated from the more fixed ones. Aqua regia attacks and decomposes the sulphides as readily as gaseous chlorine; and a mixture of hydrochloric acid and chlorate of potash is equally effectual in decomposing them. With the exception of sulphide of mercury, they are also decomposed by nitric acid, sulphuric acid and nitrate of the metal being formed; during this operation part of the sulphur is often separated in the form of tough elastic masses, which, if the heat be continued, collect into yellow globules, and can be oxidized only by prolonged digestion in the acid.

Before the blowpipe, the sulphides are easily recognised by the odour of sulphurous acid which they emit, either when heated in a glass tube open at both ends, or when roasted upon charcoal. Some other particulars relating to the sulphides have been already mentioned (356).

Preparation.—Many methods for preparing the sulphides may be adopted. 1.—Sulphur may be heated with the metallic oxides, many of which it decomposes: with the alkalies and the alkaline earths, a sulphate, and a sulphide with variable proportions of sulphur, are obtained: but when definite and pure sulphides are required, other means should be adopted. 2.—The protosulphides of the metals of the alkalies and alkaline earths may be pro-

cured by decomposing their sulphates by igniting them in closed vessels with charcoal; oxygen is removed, carbonic oxide formed, and the remaining sulphide may be dissolved in water and freed from the excess of charcoal; $KO,SO_3 + 4\,C = KS + 4\,CO$. 3.—Hydrogen is sometimes employed for preparing the sulphides from the sulphates, which are to be placed in a tube and ignited in a current of the gas. In this manner the protosulphides of the alkalifiable metals are easily obtained, but the sulphates of the other metals frequently lose a portion of sulphur, as well as all their oxygen, and subsulphides are procured. 4.—Many of the metals combine directly with sulphur, if heated with it, and form sulphides; but the compounds thus obtained often contain sulphur dissolved in, or disseminated through, the mass. Sulphide of iron is usually prepared in this manner. Indeed, sulphur, though itself combustible, supports the combustion of many metallic bodies, which burn vividly when heated in its vapour. 5.—Hydrated sulphides of the metals may also be procured, with the exception of those of the first four groups, by passing a stream of sulphuretted hydrogen through neutral or acid solutions of their salts, when they are precipitated in the insoluble form. 6.—The hydrated sulphides of zinc, iron, manganese, cobalt, and nickel, which are not thrown down by sulphuretted hydrogen, may be prepared by double decomposition, by mixing a solution of the salts of any of these metals with that of a sulphide of one of the alkalifiable metals: thus sulphate of manganese if mixed with sulphide of potassium yields sulphate of potash and sulphide of manganese; $MnO, SO_3 + HO, KS = KO,SO_3 + HO,MnS$. In many cases the colours of these hydrated sulphides are characteristic of the metal:—for example, the hydrated sulphide of zinc is white; that of manganese flesh-red; those of cadmium, arsenic, and persulphide of tin are yellow; that of tersulphide of antimony is orange-red, and that of the hydrated protosulphide of tin is chocolate-brown. The sulphides of molybdenum, rhodium, iridium, and osmium are brown, each with its peculiar shade; whilst in a large number of instances—including the sulphides of iron, cobalt, nickel, uranium, vanadium, bismuth, copper, lead, silver, mercury, gold, platinum, and palladium—the precipitated sulphides are of a black, more or less pure.

(443) *Estimation of Sulphur in Metallic Sulphides.*—Sulphur is always estimated in the form either of sulphuric acid or of free sulphur. The sulphur in a sulphide is easily converted into sulphuric acid by the agency either of gaseous chlorine or of aqua regia; and the soluble sulphates, when mixed in slightly acid solution with a salt of baryta, yield an insoluble sulphate of baryta, the

amount of which, after it has been well washed with boiling water and ignited, furnishes data for the calculation of the sulphur; 100 parts of sulphate baryta containing 34·34 of sulphuric acid, or 13·74 of sulphur. If a salt of silver be present, nitrate of baryta must be employed to precipitate the sulphuric acid.

If during the solution of a sulphide in aqua regia, the sulphur have collected into clear yellow balls, and the action upon the ore appears to be complete, it is not necessary to wait till the whole of the sulphur is dissolved: the undissolved portion may be collected on a small counterpoised filter, and weighed, and its amount must be added to that which has been converted into sulphuric acid, the proportion of which is to be ascertained by means of a baryta salt in the manner above described.

(443 *a*) The selenides and tellurides are closely analogous to the sulphides in general characters, but they are too rare to need particular description. The presence of selenium in a compound is readily ascertained by the peculiar odour which it emits when heated in the reducing flame of the blowpipe.

(444) Chlorides.—In colour and external appearance the metallic chlorides exhibit considerable variety. They are generally solid, but a few of them, such as the bichloride of tin and of titanium, the terchloride of arsenic, and the pentachloride of antimony, are liquid at ordinary temperatures. Nearly all the metallic chlorides undergo fusion at a heat attained without difficulty, many of them being partially volatilized in the operation; but the chlorides of gold, of platinum, of palladium, and of iridium, are decomposed by ignition, the metals remaining in the uncombined form. The chlorides of the other metals are not decomposed by heat when heated in closed vessels. Many of the chlorides are semi-transparent after fusion: in general they are sectile compounds, and possess but an inferior degree of hardness. In the solid form they are non-conductors of electricity, but the protochlorides, when fused, transmit the voltaic current, and experience decomposition. The action of chlorine upon the metals is generally stronger than that of oxygen upon them; but if a metallic chloride be heated in a current of oxygen or of atmospheric air, the chlorine is expelled, and an oxide of the metal is produced. The only instances in which this decomposition does not take place, occur in the case of the chlorides of the noble metals and in those belonging to the first and second groups. Chloride of magnesium is, however, readily decomposed in this manner.

In the case of the metals which have but slight affinity for

oxygen, the chlorides generally correspond in number with the oxides; and for every chloride an analogous oxide is always obtainable; but when the metal exhibits a strong affinity for oxygen, and forms a powerful base, the number of oxides frequently exceeds that of the chlorides. When mixed with water, the chlorides of some of the acidifiable metals are decomposed. In such cases it sometimes happens that hydrochloric acid and the metallic acid are formed, as occurs when chloride of tungsten or the pentachloride of antimony is mixed with a large quantity of water; for example, $SbCl_5 + 5\ HO$ becomes $SbO_5 + 5\ HCl$. In other cases, the chloride is only partially decomposed, and a portion of it unites with the newly formed oxide, thus producing an oxychloride of the metal, whilst hydrochloric acid is set free. Terchloride of antimony, and chloride of bismuth furnish instances of this kind: thus, $3\ BiCl_3 + 9\ HO = BiCl_3,\ 2\ (BiO_3, 3\ HO) + 6\ HCl$. From these cases it has been argued by some chemists that all chlorides, when put into water, decompose that liquid, and that when they remain dissolved a hydrochlorate of the oxide is formed. There are strong reasons, however, for doubting the general applicability of this view: it is found, for instance, that in many cases, on crystallization, the anhydrous chloride is separated from the aqueous solution, as occurs with common salt: and when the chloride of the metal is insoluble it is precipitated at the moment of its formation, not as the hydrochlorate, but as the anhydrous chloride; thus chloride of silver, subchloride of mercury, and chloride of lead are deposited as anhydrous chlorides, not as hydrochlorates, on the addition of a solution of hydrochloric acid, or of common salt to one of nitrate of silver, of subnitrate of mercury, or of nitrate of lead.

In many cases chlorine unites with the oxides of the metals. If the oxide of the metal be soluble in water, the *oxychloride* which is formed is soluble likewise, and the compound is remarkable for its bleaching properties. Chloride of lime ($CaOCl$), and chloride of potash ($KOCl$), furnish instances of this kind. Sometimes the chloride of a metal combines with its oxide and forms an insoluble oxychloride, as is the case with the oxychloride of mercury ($3\ HgO,HgCl$). It is a still more frequent occurrence that a chloride of one of the alkalifiable metals combines with a chloride of one of those metals which have a feebler attraction for oxygen, and the oxides of which partake rather of the character of acids than of bases. Thus we have a double chloride of platinum and potassium ($KCl,PtCl_2$) and a double chloride of gold and sodium ($NaCl,AuCl_3 + 4\ Aq$).

Preparation.—1. Many of the metallic chlorides may be formed

by heating the metal in a current of dry chlorine: in this way the perchlorides of antimony and iron are procured. 2.—If the basic oxides be heated to redness in a current of dry chlorine, oxygen is expelled and a chloride of the metal remains; but this process is never adopted for procuring the chlorides. 3.—The sulphides are generally more readily decomposed by a current of gaseous chlorine than the oxides: owing to the strong affinity of chlorine for sulphur, both the sulphur and the metal combine with the gas, chloride of sulphur, and a metallic chloride being produced. This process, however, is seldom employed except in the course of an analysis. 4.—In cases where the chloride is volatile, like that of aluminum, of glucinum, and of titanium, the oxide of the metal is mixed with charcoal, and a current of dry chlorine is transmitted over the mixture; the charcoal removes the oxygen in the form of carbonic oxide, and the chlorine, uniting with the metal, forms a chloride which volatilizes and becomes condensed in the cool part of the apparatus. 5.—In many cases the chloride may be obtained by transmitting dry hydrochloric acid gas over the oxide or the sulphide of the metal heated to low redness, the affinity of hydrogen for oxygen and for sulphur greatly facilitating the progress of the decomposition. 6.—An easier method, in cases where it is applicable, consists in dissolving the metal itself, its oxide, or its carbonate, in hydrochloric acid, and evaporating the solution to dryness, or till crystallization commences. Chloride of cobalt, of nickel, and of calcium may be thus obtained. This process, however, fails in many cases, particularly in the class to which the earths belong; chlorides of magnesium and aluminum, for example, lose their chlorine when their solutions are evaporated in contact with the air or with oxygen. 7.—In some cases chlorides of the metals, such as those of gold and platinum, are obtained by dissolving the metal in aqua regia, and decomposing any excess of nitric acid by evaporation with an excess of hydrochloric acid; a pure chloride of the metal may be obtained on re-dissolving the residue in water. 8.—Many of the chlorides of the more electronegative metals are decomposed when heated with the more basylous metals. Bichloride of tin may thus be obtained by heating metallic tin with an excess of corrosive sublimate; and terchlorides of antimony and bismuth may be obtained in a similar manner. Sometimes this process is employed for the purpose of isolating those metals the oxides of which resist decomposition by the usual means. In this way sodium is employed to decompose the chloride of aluminum or of magnesium for the purpose of procuring the aluminum or magnesium in an uncombined form; and in a

similar manner potassium is employed to decompose the protochloride of uranium. 9.—The insoluble chlorides, such as those of silver and lead, and subchloride of mercury, may be formed by the addition of hydrochloric acid, or of a soluble chloride, to a solution of the salts of these metals.

Decompositions.—All the metallic chlorides, excepting those of the metals of the alkalies and earths, are reduced when sufficiently heated in a brisk current of hydrogen. In many cases the reduction is easily effected, and this process is occasionally resorted to as a means of procuring certain metals in a state of purity. Iron, for example, may be obtained in fine cubic crystals by reducing the protochloride of the metal in this manner. It is necessary, however, to maintain a current of hydrogen of sufficient rapidity to carry away the hydrochloric acid from the reduced metal, as otherwise, in most cases, the chloride would be reproduced by the decomposition of the acid. All the soluble chlorides, when heated with sulphuric acid and black oxide of manganese, evolve chlorine gas. Other particulars relating to the chlorides have been already mentioned (313, 316).

(445) *Estimation of Chlorine in Metallic Chlorides.*—Chlorine is almost always estimated in the form of chloride of silver, 100 parts of which represent 24·74 of chlorine. The solution should be acidulated with nitric acid, and gently warmed, and then the nitrate of silver should be added. If iodine or bromine be present, it will be precipitated with the chlorine, and must be determined separately, and the corresponding weight of iodide or bromide of silver deducted.

The composition of an insoluble chloride or of a basic chloride may be determined by boiling a given weight of the compound with a pure solution of potash, and then determining the quantity of chlorine in the alkaline solution by means of nitrate of silver: before adding the solution of silver, the alkaline liquid must be filtered from the undissolved metallic oxide, and acidulated with nitric acid.

(446) The Bromides (328, 329) closely resemble the chlorides in chemical characters: the bromides of the metals of the alkalies and alkaline earths may be prepared by digesting a solution of the alkali or of the earth with bromine in slight excess; a bromide and a bromate of the metal are thus formed, and by gentle ignition the bromate is decomposed, leaving a pure bromide: a small quantity of charcoal may be added previously to the ignition, by which the decomposition of the bromate is more easily effected. The bromide is removed from the excess of charcoal by solution in water. The other bromides may be procured by acting upon the metals by

bromine, either in a dry state, or in the presence of water. They are also easily formed by dissolving the oxides or the carbonates in hydrobromic acid.

Bromine may be precipitated from its solutions, and, in the absence of chlorine, its quantity may be estimated, by means of nitrate of silver, which occasions a white precipitate of bromide of silver, 100 parts of which contain 41·47 of bromine. If chlorine be present, the precipitate will consist of a mixture of the bromide and chloride of silver: it must be collected and weighed, then digested with metallic zinc, and a drop or two of sulphuric acid; in a day or two the zinc will have reduced the bromide and chloride to metallic silver; this must be well washed, dried, and weighed. It should be wholly soluble in nitric acid, since if it be not, a portion of the precipitate has escaped decomposition.

From the above data the relative proportions of the bromide and chloride of silver may be calculated:—let m be the weight of the mixed bromide and chloride, and let s be the weight of the reduced silver; then if x represent the proportion of bromide, and y that of chloride of silver, it will be found that

$$m = x + y, \text{ and } s = \frac{108}{143{\cdot}5}x + \frac{108}{188}y;$$

consequently x, or the bromide of silver in the mixture, $= m - y$; and y, or the chloride of silver in the mixture, $= 5{\cdot}6134\,s - 3{\cdot}2247\,m$.

(446 *a*) The IODIDES (332) may be formed by processes analogous to those employed for the bromides: the insoluble iodides, such as those of silver and lead, may be obtained from a solution of iodide of potassium, by mixing it with a solution of the metallic salt.

The iodides exhibit a strong tendency to form double salts, the iodides of the strongly basylous metals combining readily to form crystallizable double iodides with those of the electro-negative metals, such as those of silver, mercury, and lead. The iodides also form double compounds with the oxides and chlorides; for example, there are several compounds of the iodide with the oxide of lead; and a combination of bichloride of tin with the protiodide of that metal ($SnI,SnCl_2$) may be obtained in orange-coloured crystals.

The quantity of iodine in a solution which contains iodides, if chlorides be absent, may be estimated by the addition of nitrate of silver slightly acidulated with nitric acid: the resulting buff-coloured iodide of silver, when collected and dried, contains 54·0

per cent. of iodine. If chlorine or bromine be present, the iodine must be precipitated by means of nitrate of palladium; the precipitate must be allowed to subside during ten or twelve hours, and it may then be collected on a filter: this precipitate is insoluble in cold diluted nitric or hydrochloric acid, but soluble in ammonia. It contains 70·0 per cent. of iodine. Iodine may also be separated from bromine and chlorine, but less perfectly, by a mixture of protosulphate of iron and sulphate of copper (744).

(447) Fluorides.—The general properties of these compounds have been already stated (338). The fluorides are usually prepared by the direct combination of hydrofluoric acid with the metallic oxide. Those which are insoluble may be procured by mixing a solution of the metallic salt with one of fluoride of potassium or of sodium.

Estimation of Fluorine.—A simple method of detecting and of approximatively estimating fluorine, when present, even in very small quantities, has been proposed by Dr. G. Wilson. The following is the process, slightly modified:—the substance, if it does not already contain silica, is mixed with pounded glass, placed in a retort, and made into a thin cream with oil of vitriol; the mixture is next heated, and distilled into a flask containing a solution of ammonia; the fluoride of silicon comes over, and is immediately decomposed: on evaporating the liquid in the flask to dryness on a water-bath, the silica is rendered insoluble, and can be collected and weighed, whilst the fluoride of ammonium may be dissolved out with a little water, and the presence of fluorine shown by mixing it with oil of vitriol; the vapour which is evolved produces the usual corrosive action of hydrofluoric acid on glass (338): the proportion of silica in the insoluble residue to the fluorine, however, is not very uniform.

(448) Nitrides.—It is not improbable that the fulminating compounds, obtained by digesting the hydrated oxides of gold, of silver, and of platinum, in a solution of ammonia, may owe their explosive character to the formation of a nitride: the composition of these bodies has, however, been but imperfectly investigated, on account of the ease with which they explode. So weak is the affinity of nitrogen for most metallic bodies, that a slight alteration of circumstances often suffices to restore it suddenly to the gaseous state. Nitride of copper is formed by passing dry ammonia over oxide of copper, at a temperature not exceeding 480°, in which case water is formed at the expense of the hydrogen of the ammonia and the oxygen of the oxide, and part of the nitrogen escapes; thus, $6\ CuO + 2\ H_3N = Cu_6N + 6\ HO + N$. Nitride of mercury may be

repared by passing ammonia over oxide of mercury in a similar nanner. Titanium, molybdenum, and vanadium absorb nitrogen apidly at a red heat.

(449) The PHOSPHIDES of the metals are of comparatively mall importance: they are never met with in the native state. he phosphides of the metals of the alkalies and alkaline earths ecompose water when thrown into it; self-lighting phosphuretted ydrogen is disengaged, and a hypophosphite of the base is retained n solution. In some cases, as for example in that of phosphide of alcium, the phosphide is formed by heating the oxide strongly, and riving the vapour of phosphorus over it; in this case it is mixed ith a large proportion of phosphate of lime. The insoluble phoshides may often be obtained by transmitting a current of phoshuretted hydrogen through a solution of the salt of the metal in ater: phosphides of copper and silver may be thus obtained.

When heated in air the phosphides are converted into phoshates, or into phosphoric acid, while the metal is liberated.

(450) CARBIDES.—The only carbides of importance are those of on, which will be considered in detail when treating of that metal. langanese, palladium, iridium, and a few other metals, also comine with carbon; generally speaking, these carbides are more usible than the metals which enter into their formation.

SILICON AND BORON form with the metals analogous compounds f small importance.

(451) HYDRIDES.—Hydrogen is not known to combine with ore than four metals: viz., arsenic, antimony, copper, and otassium. The first two of these compounds are gaseous, and e decomposed by a red heat into metal and hydrogen gas. A olid hydride of arsenic is also said to exist. A few metals, such s zinc and potassium, appear under peculiar circumstances to ndergo partial volatilization along with the hydrogen at the oment that this gas is evolved.

§ III. THEORY OF SALTS.

(452) *Acids and Bases.*—It has already been stated (6) that ny substance which is produced by the union of a base with an cid is termed a salt. It is, however, necessary to examine more inutely into the nature both of bases and of acids, and into at of the compounds formed by their combination with each her.

By the word *base,* is meant a body always of a compound ature, very frequently an oxide of a metal, which is capable of

uniting with an acid, and of more or less completely neutralizing the distinctive characters of that acid. A base, however, is not necessarily a metallic oxide; ammonia, quinia, and morphia, for example, are powerful bases, but they contain no metallic substance.

Besides the class of salts formed by the combination of an acid with a base, there is a numerous and important series in which neither acid nor base is present, and of which common salt is a familiar instance. We proceed to indicate the points of difference and agreement between these two kinds of salts.

(453) *Oxyacids and Hydracids.*—When Lavoisier imposed the name of oxygen upon one of the constituents of the atmosphere, he supposed that the presence of that energetic body was essential to the existence of an acid; and this view was supported by the known composition of the principal acids, such as the sulphuric, the sulphurous, the nitric, the carbonic, the phosphoric, and the boracic acids. An acid was then considered to be an oxidized body more or less soluble in water, with a sour taste, capable of reddening vegetable blues, and entering into combination with the alkalies, the distinctive properties of which it neutralized.

By degrees, however, acids were discovered in which no oxygen could be detected: such, for example, as the hydrochloric, the hydriodic, and the hydrobromic, into the composition of which hydrogen enters; yet these bodies were found in other respects to correspond perfectly with the above definition, and to possess all the characters of powerful acids. To meet this objection, the theory was modified, and the acids were divided into two great classes, the first of which comprised the *oxyacids*, such as the sulphuric, nitric, and others of analogous composition, in which it was supposed that the acid properties depended on the presence of oxygen; the second class was formed by the *hydracids*, such as the hydrochloric and hydriodic acids, in which the acidifying principle was assumed to be hydrogen. It was noticed, that when bodies belonging to either of these classes combine with metallic compounds, and form neutral combinations, the acids do not unite directly with the metals; the combination is always with their *oxides*: sulphuric acid, for example, has no action upon metallic copper, but it quickly dissolves its oxide, forming the blue solution of sulphate of oxide of copper. On applying heat so as to render the salt anhydrous, it was found that the salts of the oxyacids (of which sulphate of potash, KO,SO_3, may be taken as the type) might be represented under the form MO,SO_3, which supposes the union of 1 equivalent of the dry acid with 1 equivalent of a

metallic oxide; while a hydracid (such for instance as hydrochloric acid) if united with a base such as soda, yields a body like common salt (NaCl), which when dry contains neither hydrochloric acid nor soda, the radicle of the acid being left in combination with the metal itself: $NaO + HCl$ yielding $NaCl + HO$. Thus, in the case of the salts of the hydracids, it will be observed that the oxygen of the oxide is precisely sufficient to convert the hydrogen of the acid into water: this union, indeed, actually takes place, and the water so formed is expelled on the application of heat. It thus appears that although compounds produced by the union of an acid with a base, may be correctly designated salts, it would lead to a strange anomaly were the term salt to be confined to compounds formed by the combination of any acid with a base, since such a definition would exclude common table-salt—the very substance from which the term salt was originally derived: table-salt, it is true, may be formed by the union of hydrochloric acid with the base, soda, but the compound when dry contains neither the acid nor the alkali which was used.

To obviate this difficulty, it was proposed to subdivide salts into two classes,—the first, like nitrate of potash, being formed by the union of an oxide, such as potash with an oxyacid such as the nitric; these were termed *oxysalts*: the other class being produced by the combination of a metal with the characteristic element in a hydrogen acid. The salts of the second class, being composed upon the same plan or type as sea-salt, were termed *haloid* salts (from ἅλς, 'the sea'). This distinction is generally recognised by chemical writers of the present day.

(454) *Binary Theory of Salts.*—The foregoing observations seem to prove that there is a marked difference between the composition of the oxyacid and the hydracid series of salts. The separation of salts into two classes, one consisting of the salts of the oxyacids, and the other of those of the hydracids, is not, however, indispensable. A hypothesis was advanced by Davy, which reduces all salts under one class, and refers them all to the hydracid type. Upon this view—frequently termed *the binary theory* of salts—all the hydrated acids are regarded as salts containing hydrogen in the place of a metal, so that oxide of hydrogen, or water, acts the part of a feeble base to the anhydrous acids. It is remarkable that those of the oxyacids which can be obtained in the anhydrous form, such for example as the sulphuric, the nitric, the phosphoric, the carbonic, and the boracic anhydrides, do not possess the properties generally admitted to constitute the true acid character. Sulphuric anhydride, for instance,

does not redden dry litmus; it may be moulded in the fingers without injury; but when once it has passed into the hydrated form, which it speedily does by absorbing moisture from the air, it corrodes all organized substances with great activity. Dry carbonic acid is also without action on litmus. When such compounds have entered into combination with water they may be represented as hydracids by a slight modification of the ordinary formula; *e.g.*, nitric acid (HO,NO_5) may be expressed as (H,NO_6), corresponding with hydrochloric acid (H,Cl): each atom of their hydrates, when heated in contact with a base or a metallic oxide, gives off 1 atom of water, in a manner precisely analogous to the hydracids already examined. One equivalent of oil of vitriol treated with 1 equivalent of oxide of lead would thus produce an equivalent of sulphate of lead and an equivalent of water; $H,SO_4 + PbO$ becoming $Pb,SO_4 + HO$.

Upon this theory, the compounds which chemists have been in the habit of considering as hydrated acids, would be regarded as salts composed of a compound radicle (consisting of the anhydrous acid + an equivalent of oxygen) united with an equivalent of hydrogen. The other salts of the acid would be formed from these hydrogen compounds by the displacement of the hydrogen by an equivalent amount of each of the different metals which enter into the composition of the various salts, and which are indicated by their respective names. A very simple explanation is in this manner afforded of the liberation of hydrogen when diluted sulphuric acid is acted upon by zinc; the zinc simply entering into combination with the radicle of the acid, and displacing the hydrogen; thus $HSO_4 + Zn$ become $ZnSO_4 + H$; and the reaction is, upon this view, perfectly analogous to that of the same metal upon hydrochloric acid; $HCl + Zn = ZnCl + H$.

This elegant hypothesis long remained an unsupported and fruitless speculation; but the researches made in the department of organic chemistry have increased its probability; and it has also in particular cases received direct experimental confirmation from the voltaic researches of Daniell. It was found by Mr. Daniell and myself, that if a current of voltaic electricity from two or three cells of Grove's construction were transmitted through fused nitrate of silver, the salt was readily decomposed, but that metallic silver in crystals was deposited upon the platinode, whilst the oxygen and the nitric acid passed to the zincode, so that under these circumstances, the nitrate of silver (AgO,NO_5) was resolved into Ag and NO_6; the NO_6 breaking up at the moment of its liberation into red fumes of peroxide of nitrogen and free oxygen gas. Other

experiments which further illustrate this point will be described hereafter (868).

A good instance of the advantageous application of Davy's theory is afforded by the different modifications of phosphoric acid, the leading peculiarities of which have been already described (369). For example, the formulæ of the three different varieties of phosphate of soda, when represented upon the ordinary view of their composition, may be thus contrasted with those of the same salts upon the binary theory, omitting their water of crystallization:—

	Ordinary view.	Binary view.
Metaphosphate of soda	NaO,PO_5	Na,PO_6
Pyrophosphate of soda	$2\,NaO,PO_5$	Na_2,PO_7
Tribasic phosphate of soda . . .	$3\,NaO,PO_5$	Na_3,PO_8.

Each modification of the acid forms a corresponding phosphate with hydrogen, the three compounds with hydrogen being usually considered as three distinct hydrates of phosphoric acid, or phosphates of water; but which may be represented upon either view, for example:—

	Ordinary view.	Binary view.
Metaphosphate of water	HO,PO_5.	H,PO_6
Pyrophosphate of water	$2\,HO,PO_5$	H_2,PO_7
Ordinary phosphate of water . .	$3\,HO,PO_5$	H_3,PO_8.

Much difficulty in comprehending the anomalous relation of phosphoric acid to water is removed if each modification be considered to possess a different radicle, which regulates the varying constitution of the three classes of salts; a view which is found not to be inconsistent with the results of voltaic decomposition, which indeed are most readily explained by its assumption (Daniell and Miller, *Phil. Trans.*, 1844, p. 4). Upon this theory it is evident that so long as each radicle possesses its peculiar constitution, it will require its own characteristic number of atoms of base to form a salt; on the old hypothesis, however, there appears to be no satisfactory reason why, in the aqueous solutions of the acid, sometimes one atom, sometimes two, and sometimes three atoms of water should be displaced by a corresponding number of equivalents of a base. In order to render this evident, it must be remembered that water, when in combination, plays several distinct parts (291). The water, chemically united with these hydrates of phosphoric acid, acts the part of a base, and is in a condition very different from the *water of crystallization* which many crystallized salts contain in the dry or solid form, and which is essential to the possession of their peculiar crystalline shape.

Ordinary rhombic phosphate of soda presents water acting both as a base and as water of crystallization. The constitution of

this salt may be represented by the formula (Na_2H,PO_8+24 Aq). The 24 atoms of water of crystallization are expelled by a temperature below 300° F. If the residue be dissolved in water, the solution presents all the characters of a solution of the original salt, and by evaporation the phosphate of soda is recovered in its original crystalline form. If, however, the dry residue, Na_2H,PO_8, be heated to redness, an additional atom of water escapes; the radicle, PO_8, is partially deoxidized by the hydrogen; a new radicle, PO_7, is formed, and enters into combination with Na_2; Na_2H,PO_8 becomes Na_2,PO_7+HO; and on dissolving the residue after ignition in water, a new salt, the pyrophosphate of soda, is produced. In like manner, if the acid phosphate of soda, NaH_2,PO_8, be heated to redness, the two atoms of hydrogen remove two equivalents of oxygen from the radicle, PO_8, which then becomes PO_6; $NaH_2,PO_8=Na,PO_6+2\,HO$.

Binary compounds are such as consist of two elements only; chloride of sodium (NaCl), therefore, is a binary compound; and if all salts be assimilated to this type, it is assumed that the grouping of their molecules resembles that which occurs in this binary compound. Upon this view all salts consist of two portions: one comprising the distinctive constituents of the acid, and consisting either of a non-metallic elementary substance (chlorine, Cl, for example), or else an equivalent compound body (such as sulphion, SO_4), which is termed the *radicle* of the salt; the other is either a metal (sodium, Na, for instance), or else a compound like ammonium (H_4N), equivalent to a metal, and which Graham calls the *basyl* of the salt. The hydrated acids are regarded merely as salts of hydrogen, which in combination comports itself like a metal, and which, for aught that is known to the contrary, may really be a metallic vapour.

(455) *Objections to the Binary Theory.*—Notwithstanding the ingenuity of the foregoing theory, and the advantages which it offers in the explanation of certain modes of decomposition, it is open to many serious objections; and indeed it cannot be regarded as a correct representation of the composition of a salt under all circumstances.

A few of these objections may be pointed out:—

1. None of the compound radicles, SO_4,NO_6,CO_3, have been obtained in an isolated form, nor is it probable that they ever will be.

2. It appears to be highly improbable that a body of such powerful affinities as potash should, in carbonate of potash for example, part with its oxygen to a substance which, like carbonic

acid, exhibits no tendency to further oxidation, so that KO,CO_2 should become K,CO_3.

3. Further, if this theory be applied to the ordinary salts of the oxyacids, no reason can be assigned why it should not be equally applicable to the corresponding sulphur compounds, and then the contradictions and inconsistencies arising from its application become still more apparent.

The conclusion which a careful review of the arguments adduced seems to render most probable is this: viz., that a salt, when once formed, must be regarded as a whole; it can no longer be looked upon as consisting of two distinct parts, but as a new substance, maintained in its existing condition by the mutual actions of all the elements which compose it. These different elements are not all united with each other in every direction with an equal amount of force. As in a crystal there are certain directions in which the mass admits of cleavage with greater facility than in others, and as two or three different directions of cleavage may be found in the same crystal by varying the direction in which the force is applied, so in the same salt there are directions in which it yields to the application of chemical force more readily than others; and according as that chemical force is applied in one way or in another, the compound splits up into simpler substances, the nature of which will vary according to the mode which has been selected for effecting its decomposition.

For example, if the solution of a powerful acid, such as nitric acid, be poured upon carbonate of potash, carbonic acid is liberated abundantly, and nitrate of potash is produced; $KO,CO_2+HO,NO_5=KO,NO_5+CO_2+HO$; but if another portion of the same carbonate of potash be mixed with charcoal, and heated in an iron retort to whiteness, metallic potassium and carbonic oxide are the results; $KO,CO_2+2\ C=K+3\ CO$. Again, if a solution of carbonate of potash be subjected to electrolysis by the aid of the voltaic battery, the salt splits up into potassium (which is immediately oxidized by the water in the midst of which it is liberated), and into CO_3, which is as instantly resolved into oxygen gas and carbonic acid; KO,CO_2 becoming $K+CO_3$, and $K+HO$ giving $KO+H$, whilst CO_3 becomes CO_2+O. The probability therefore is, that neither the old nor the new view is absolutely correct, but that each may in turn well represent the salt when subjected to the influence of particular circumstances. It may therefore readily be conceded that the binary theory may in certain cases elucidate the decompositions observed, notwith-

standing the difficulties which prevent its adoption as a correct representation of the molecular arrangement of saline compounds in general when in a quiescent state.

(456) *Sulpho-Salts.*—The preceding remarks have been made with almost exclusive reference to those salts into the composition of which oxygen enters. There is, however, a numerous series of compounds parallel to these oxy-compounds, but in which sulphur enters into combination with the metal; and for each atom of oxygen in the series of the oxy-salts an equivalent of sulphur is substituted in the corresponding compound in the sulphur series. Generally speaking, the sulphur-salts are of subordinate importance to the oxy-compounds; they are often decomposed by water, and have been the subject of much less study and research. Many chemists regard these compounds as salts in which the electro-positive sulphides, such as the protosulphide of potassium, &c., act the part of bases; and the electro-negative sulphides, such as the higher sulphides of arsenic and antimony, act as acids.

(457) *Varieties of Salts.*—Salts are usually spoken of as *neutral*, *acid*, or *basic*; but though these terms are in general use, there is some ambiguity in the manner in which they are applied.

(458) *Neutral*, or *Normal Salts.*—The idea of neutrality implies that the peculiar characters of the acid and of the alkali have each disappeared as a result of combination, and one of the usual means by which this neutralization in properties is judged of consists in observing the effect which is produced upon certain vegetable colours when mixed with a solution of the salt.

The blue colour of litmus, for example, is changed to red by the action of an acid, whilst the colour of litmus reddened by an acid becomes blue if it be mixed with an alkali. The yellow colour of turmeric is changed to brown when mixed with an alkali, but the yellow is restored if the alkali be caused to combine with an acid. A salt which affects neither the blue of litmus nor the yellow of turmeric is said to have a neutral reaction. But chemists are in the habit of regarding many salts as neutral in composition which are not neutral in their action upon coloured tests. The basic properties of different metallic oxides vary considerably in intensity. Equal quantities of the same acid, according as it is neutralized by equivalent quantities of a weak base or of a strong one, will differ considerably in their action upon coloured tests: for example, 54 parts of nitric acid in combination with 47 parts of potash furnish nitrate of potash, which, when dissolved in water, does not affect the colour either of blue or of reddened litmus paper. It is therefore

neutral in its reactions upon coloured tests. In the case of nitrate of potash, the proportion of oxygen in the potash to that in the nitric acid is as 8 parts to 40, or as 1 atom is to 5.

Salts of nitric acid in which the oxygen of the base bears this proportion to that in the acid, are regarded as neutral in composition, whatever may be their action on vegetable colours. Now if the same proportion of nitric acid be caused to combine with an equivalent of oxide of lead, 112 parts of oxide of lead will combine with the 54 of nitric acid, and will form a salt in which, as in nitrate of potash, 1 atom of oxygen is present in the base for every 5 atoms of oxygen in the acid. This salt, therefore, is neutral in composition, though if dissolved in water it reddens litmus, and has an acid reaction. The same thing is true, also, in the case of nitrate of copper.

The change in the tint of the coloured test is therefore not to be regarded as an absolute proof of neutrality or acidity in a salt. The change of colour which the litmus experiences, even from a salt of neutral composition, is readily explained. Blue litmus is itself a species of salt, formed by the combination of an alkaline or earthy base with a feeble vegetable acid which is naturally of a red colour, but which becomes blue when it is neutralized by an alkali. When a powerful acid, such as the nitric or the sulphuric, is mixed with this blue colouring matter, the strong acid seizes upon the base which the litmus contains, and displaces the litmus acid which appears of its natural red hue; but on the addition of an alkali, the blue is restored by the combination of the newly added base with the litmus acid. Again, if a salt with a strong acid and a comparatively feeble base be mixed with the blue litmus, the strong acid of the salt seizes upon part of the base which is in combination with the litmus, and liberates the litmus acid, which appears of a more or less intense red, according as the base of the neutral salt has given up more or less of its acid.

For analogous reasons it sometimes happens that a salt which is neutral in composition may exhibit characters in which the base preponderates to a greater or less extent. Carbonate of potash (KO,CO_2) is neutral in composition, but it appears to be basic in its action upon the yellow colour of turmeric paper, which it renders powerfully brown, and it immediately restores the blue tinge to reddened litmus. This ambiguity in the use of the word neutral, may, however, be entirely obviated by describing as *normal salts* the salts above-mentioned as neutral in composition; employing the term neutral solely with reference to the action of the body upon coloured tests, and in this sense we shall hereafter use these terms.

The three salts which have just been cited to illustrate these points are all of them instances of the most usual form of salt, in which 1 atom of a protoxide is united with 1 atom of an acid to form the normal salt. But salts exist in which the base consists of a sesquioxide, and in such cases 3 atoms of the acid are needed to 1 atom of the base in order to produce a normal salt.

The sulphates afford a good illustration of these different modes of combination. A normal sulphate of a protoxide, such as sulphate of potash (KO,SO_3) requires 1 equivalent of oxygen in the base to 3 equivalents of oxygen in the acid; and contains 1 equivalent of acid to each equivalent of the base.

But in the case of a sesquioxide,* such as alumina, Al_2O_3, 3 atoms of acid are combined with each atom of alumina in order to form the normal sulphate of this base, $Al_2O_3, 3\ SO_3$; and the normal sulphate of peroxide of iron ($Fe_2O_3, 3\ SO_3$) has a similar composition: in salts of this kind, however, the rule is still observed, that the number of atoms of oxygen in the base is to that of those in the acid as 1 to 3. The sulphate of alumina and the persulphate of iron not only redden litmus paper powerfully, but they have an acid as well as an astringent taste.†

* It is a common but incorrect practice, when treating of a sesquioxide, to regard the sum obtained by adding together the atomic weights of its several constituents, as furnishing the *chemical equivalent* of the sesquioxide. For example, the composition of the compound atom of alumina is regarded as Al_2O_3, and its chemical equivalent is commonly represented as 51. It has already been stated (*note*, p. 20, Part I., and p. 3, Part II.) that the *equivalent* of any substance is really the quantity of that substance which is capable of supplying the place, in a particular compound, of some other body with which the substance is compared. Al_2O_3 is therefore correctly represented as equivalent to Fe_2O_3, since it is capable of supplying its place in combination with $3\ SO_3$; the salts ($Al_2O_3, 3\ SO_3$) and ($Fe_2O_3, 3\ SO_3$) being strictly analogous. But Al_2O_3 is not equivalent to KO, to PbO, or to CuO, in the sulphate of potash (KO,SO_3), sulphate of lead (PbO,SO_3), or sulphate of copper (CuO,SO_3); $\frac{1}{3}$ of Al_2O_3 being really the proportion in which alumina combines with each proportional of sulphuric acid in the normal sulphate. The equivalent of any substance therefore must vary according to the nature of the body with which it is compared, though its molecular composition is not liable to such variation. In order, therefore, to avoid the ambiguity and inaccuracy of calling the proportion (Al_2O_3) the equivalent of this base, when compared with a protoxide, we shall speak of it as the *atom* of the sesquioxide.

† The tendency of the sesquioxides to require so large a proportion of acid has been supposed to afford another argument in favour of the binary theory of salts. It will be seen that the composition of the normal persulphates readily admits of being represented upon the binary view in harmony with the sulphates of the protoxides. Sulphate of peroxide of iron, for example, ($Fe_2O_3, 3\ SO_3$) might be written ($Fe_2, 3\ SO_4$). This argument, however, is entitled to but little weight, because many salts of the sesquioxides are known, such as those of uranium and antimony, in which the proportion of the acid is less than in these instances; and, indeed, both alumina and peroxide of iron form, with sulphuric acid, soluble compounds which contain but 1 atom of acid to 1 atom of base.

(459) *Acid Salts.*—If a quantity of oxalic acid be divided into two equal portions, one of which is dissolved in water, and mixed with a solution of potash until the liquid becomes neutral in its reaction upon litmus, a salt is formed which, on evaporation, may be obtained crystallized in six-sided prisms, which consist of the normal oxalate of potash ($2\ KO,C_4O_6 + 2\ Aq$). If this salt be redissolved in water, and the second portion of oxalic acid be added to it, chemical union of the two bodies will occur; the liquid so obtained will be found to have a sour taste, to redden litmus powerfully, and on evaporation to yield a new salt, which crystallizes in rhomboidal prisms, containing exactly half as much potash in proportion to the acid as the first salt; this is the binoxalate, or acid oxalate, of potash ($KO,HO,C_4O_6 + 2\ Aq$).

Again, if the normal sulphate of potash (KO,SO_3) be dissolved in hot sulphuric acid, tabular plates of a new, fusible, and strongly acid salt will crystallize out as the liquid cools, and the bisulphate or acid sulphate of potash will be formed ($KO,HO,\ 2\ SO_3$). This salt contains for each atom of oxygen in the potash, 6 atoms of oxygen in the acid, or double the amount which is present in the normal sulphate. If an attempt be made to form a similar salt by dissolving nitrate of potash in nitric acid, the experiment will fail, for the nitre will be found to crystallize out unchanged.

It is thus apparent that in certain cases the acid combines with the base in two proportions, in others it refuses to do so in more than one.

It usually happens that acid salts contain, in addition to the acid and base, a certain quantity of water, as occurs for instance in the acid sulphate and the acid oxalate of potash. This water is not to be regarded in the light of water of crystallization: it discharges a more important function, for it takes the place of the metallic oxide on these occasions: and it is because the basic properties of water are so feeble, that the acid character predominates to so great a degree in such salts.

(460) *Polybasic Acids.*—The formation of acid salts may be elucidated by the following considerations. Most of the inorganic acids combine with bases in such a manner that 1 atom of the acid is united with 1 atom of a metallic oxide, so that they may be termed *monobasic acids*. Of this class of acids the nitric is a good example.

Certain acids, however, exist, of which an instance has already presented itself in the pyrophosphoric, 1 atom of which possesses the power of combining with 2 atoms of base; such acids are hence termed *dibasic*. Numerous acids of this class are found among

those obtained from the vegetable and the animal kingdoms; tartaric acid ($2\,HO,C_8H_4O_{10}$), and malic acid ($2\,HO,C_8H_4O_8$) are examples of this kind.

The common phosphoric acid contained in the crystallized phosphate of soda of commerce, is the representative of a third class of acids, 1 atom of which combines with 3 atoms of base; such acids are hence termed *tribasic*. There are many organic acids which belong to this class; of which the citric ($3\,HO,C_{12}H_5O_{11}$) furnishes a good instance.

It is not necessary that the two or the three atoms of base which the salts of the dibasic or tribasic acids contain should consist of the same metallic oxide. Indeed, it has already been shown, in the case of the various phosphates, that several bases may coexist in the same salt, in definite proportions. There is, for example, a pyrophosphate of soda and water, composed of NaO,HO,PO_5, in which 1 atom of hydrogen supplies the place of its equivalent of sodium; and in the microcosmic salt ($NaO,H_4NO,HO,PO_5 + 8\,Aq$), we have a tribasic phosphate of soda, oxide of ammonium, and water, where each of the 3 atoms of base differs from the others. It is worthy of remark that, in the salt last named, two of these bases, viz., soda and oxide of ammonium, are isomorphous.

Now it frequently happens, as in microcosmic salt, that water is one of the bases present in the salt, and, when such is the case, the salt, when dissolved in water, often has a sour taste, and reddens litmus paper strongly. It is in this way that the most common variety of acid salts is formed. Cream of tartar, or, as it is often called, bitartrate of potash, offers a good illustration of this kind of salt.

Cream of tartar is a sparingly soluble crystallizable compound, of an agreeable acidulous taste; it consists of $HO,KO,C_8H_4O_{10}$, and is, in fact, a dibasic tartrate of potash and water: if now it be dissolved in hot water, and another atomic proportion of potash be added, the water is displaced by the second atom of potash, all the acid taste disappears, and normal tartrate of potash ($2KO,C_8H_4O_{10}$), a salt which no longer affects the colour either of litmus or of turmeric paper, is produced. An equivalent quantity of carbonate of potash may be substituted for caustic potash with equal effect, as it will be decomposed, and the carbonic acid will be expelled with effervescence. Carbonate of soda may be substituted for the carbonate of potash, but in this case a different salt, known as Rochelle salt, the tartrate of soda and potash, will be formed ($KO, NaO,C_8H_4O_{10} + 8\,Aq$).

Acid salts, however, though generally formed, like cream of

tartar, from a dibasic acid with which 1 atom only of a powerful base has combined, the place of the second atom of base being supplied by an atom of water, are not always so produced. An acid sulphate of potash, which is anhydrous, may be obtained ($KO, 2\ SO_3$); and the acid chromate or bichromate of potash always occurs in the anhydrous form. Graham has endeavoured to account for the formation of some other acid salts in a different manner, which will be noticed presently.

(461) *Double Salts.*—The description of these polybasic acids has presented us with certain cases in which *double salts* are formed. There are several varieties of double salts. The most common are those which are produced by the union of two dissimilar bases with the same acid. These varieties, however, are confined within certain limits. It is not possible to form double salts *ad libitum,* by bringing 2 equivalents of any acid in contact with 1 equivalent each of any two bases. Chemists assume that when two isomorphous bases, such as soda and potash, combine with the same acid in the proportion of 1 equivalent of each base to form a double salt (like Rochelle salt), the acid in question is dibasic. The larger number of double salts which have been produced are thus formed by the combination of different bases with polybasic acids. The bicarbonates, binoxalates, and many other similar compounds, prove, on examination, not to be mere salts with excess of acid, but true double salts of this class, analogous to normal or neutral salts in composition. Bicarbonate or acid carbonate of potash, for instance, may be represented as thus constituted, KO,HO,C_2O_4; and binoxalate or acid oxalate of potash, $KO,HO,C_4O_6 + 2\ Aq$. Some other considerations relating to the basicity of acids and to the polybasic acids will be more conveniently deferred until the nature of the organic acids has been discussed (1091 *et seq.*)

The formation of another remarkable series of double salts, particularly investigated by Graham, appears to be directly connected with the mode in which water attaches itself to certain salts. In most cases the water of crystallization may be expelled from a salt by exposing it to a temperature not exceeding 212°. This, however, does not always happen: sometimes all the water of crystallization may thus be expelled with the exception of a single equivalent, which requires a much higher heat for its expulsion, although in these cases it does not appear to act in any degree as a base. Under these circumstances it was found that this last equivalent of water might readily be displaced by adding to the salt an equivalent of certain anhydrous salts. An excellent illus-

tration of such a method of the formation of double salts is afforded in the case of a certain class of the sulphates. All the sulphates of bases isomorphous with magnesia are capable of forming double salts of this nature with some anhydrous sulphate not isomorphous with this class—such, for instance, as the sulphate of potash.

When sulphate of magnesia ($MgO,SO_3,HO+6Aq$) is heated to 212°, six out of the seven atoms of water are expelled, but the seventh atom is retained until the temperature is raised considerably. If, however, sulphate of magnesia and sulphate of potash be separately dissolved in water in equivalent proportions, mixed while hot, and allowed to crystallize, a new double salt ($MgO,SO_3+KO,SO_3+6\ Aq$) is deposited, having the same crystalline form as sulphate of magnesia, but it contains only 6 atoms of water of crystallization. The seventh atom has been displaced by the sulphate of potash, and has hence been termed, by Graham, constitutional, or *saline water*.

A similar substitution takes place with sulphuric acid itself, or sulphate of water; when diluted till of the specific gravity of 1·78, it consists of (HO,SO_3+HO), and from the circumstance of its readily forming well-defined crystals when cooled to a temperature of 40°, it is often termed glacial sulphuric acid: this compound consists of 1 atom of sulphate of water with 1 of saline water. If a solution of sulphate of potash be added to this glacial acid, the liquid, when evaporated, yields the well-known acid sulphate of potash. Graham regards the latter compound, consisting of sulphate of water and sulphate of potash, as a double salt, in which the sulphate of potash has displaced the saline water from the glacial acid; $KO,SO_3+(HO,SO_3+HO)=HO+(HO,SO_3+KO,SO_3)$: the water in the acid sulphate being in the form of basic water. The formation of this salt may, however, be equally well accounted for upon the supposition that sulphuric acid is dibasic, and that the acid sulphate, or, as it is usually called, the bisulphate of potash, is a salt formed upon the type of the neutral sulphate, but containing an atom of hydrogen in the place of the second atom of potassium, thus:—

$$\overbrace{KO,KO,S_2O_6}^{\text{Neutral sulphate.}}\ ;\ \overbrace{KO,HO,S_2O_6}^{\text{Acid sulphate.}}\ ;\ \overbrace{HO,HO,S_2O_6}^{\text{Sulphuric acid.}}.$$

There is another well-known variety of double salts, in which it is not necessary that the component salts should contain similar oxides, or even a similar number of equivalents of the radicle of the acid. In this way sulphates of sesquioxides often unite with the sulphates of protoxides to form well-characterized double salts;

a striking example of this kind is afforded in the important tribe of alums. Common alum consists of 1 atom of sulphate of potash and 1 atom of sulphate of alumina with water of crystallization ($KO,SO_3 + Al_2O_3, 3\ SO_3 + 24 Aq$); and numerous other salts, having the same crystalline form, and of similar composition, might be mentioned.

There are a few instances of two different acids being united to one base, but they are neither sufficiently numerous nor important to merit lengthened notice, and are more frequently met with among natural than artificial combinations.

Instances are common in which two different haloid salts unite with each other; compounds of this description are most usual between the chlorides, iodides, and bromides of the less oxidizable metals with those of the metals contained in the alkalies and earths: the double chloride of platinum and potassium ($KCl,PtCl_2$), and the double iodide of mercury and potassium (KI,HgI), are good instances of such compounds. Bonsdorff proposed to consider these compounds in the light of salts in which the chloride or iodide of the electro-negative metal (platinum, gold, &c.) acted the part of an acid towards the electro-positive chloride (chloride of potassium, sodium, &c.); but this view is not tenable. Such salts are never resolved by electric action into their constituent chlorides, and the acid reaction of the higher chlorides is not neutralized or modified by combination with the chlorides of the alkaline metals; in fact, the constituent chlorides themselves are salts.

Many double salts may be formed by fusion with each other, although if the attempt be made to crystallize them from a solution containing equivalent quantities of the two salts, the attempt is unsuccessful. Chloride of sodium, for example, may be melted with an equivalent amount of chloride of calcium, of strontium, or of barium; and in each case a compound salt is obtained, which has a much lower fusing point than either of its component chlorides in a separate form, but the double salt is decomposed when it is dissolved in water.

(462) *Subsalts.*—A very different series of saline compounds still remains for consideration, and in these the proportion of base predominates over that of the acid; they are usually designated *basic salts*, or subsalts. The theory of the formation of these compounds is very imperfect. In certain cases the formation of a subsalt admits of the explanation offered by Graham. He assumes that a portion of the water of crystallization of the neutral salt has been displaced by a basic metallic oxide. The nitrates of copper

offer an example of this kind of displacement. Nitric acid of specific gravity 1·42 (which may be distilled without undergoing change) consists of 1 atom of the protohydrate with 3 atoms of water, which correspond to the water of crystallization in a salt ($HO,NO_5 + 3$ Aq).—Nitrate of copper contains an equal number of atoms of water of crystallization, $CuO,NO_5 + 3$ Aq. But there is also a subnitrate of copper, which represents the nitrate of copper, in which the 3 atoms of water of crystallization are displaced by 3 atoms of hydrated oxide of copper, CuO,NO_5, 3 (CuO,HO), a green compound which is left in the form of an insoluble powder, when the neutral nitrate of copper is partially decomposed by a heat of about 400°.

Water may be displaced not only from saline combinations by metallic oxides, but may be removed from certain organic compounds by oxides which take its place. For example, a compound of sugar with oxide of lead, ($C_{12}H_9O_9$, 2 PbO), may be formed from cane sugar ($C_{12}H_9O_9$, 2 HO) by boiling it with litharge; and on suspending this new compound in water, and removing the lead by means of sulphuretted hydrogen, the original quantity of water is restored, and the sugar is recovered with its characteristic properties: 2 $HS + C_{12}H_9O_9$, 2 PbO yielding 2 $PbS + (C_{12}H_9O_9$, 2 $HO)$.

The formation of many subsalts, however, is not explicable in this manner. Nitrate of lead, for example, crystallizes in anhydrous octohedra; but a crystallized dinitrate of lead may be obtained consisting of (2 $PbO,NO_5 + 2$ Aq); and a trisnitrate and hexanitrate of lead have also been obtained by Berzelius. In these cases the oxide of lead cannot be said to have taken the place of the water of crystallization of the neutral salt. All that can be said, is, that in such cases the metallic oxide attaches itself to the neutral salt in a manner analogous to that in which water of crystallization does in other instances.

The tendency to the formation of subsalts is limited to certain acids and bases: sulphuric, nitric, carbonic, and acetic acids, and the oxides of copper, of lead, of mercury, and of zinc, are the most remarkable in this respect.

(463) *Oxychlorides, &c.*—A class of compounds which resemble the subsalts more than any others, is presented to us in the bodies termed oxychlorides, oxyiodides, and oxycyanides. In these compounds, one atom of the chloride, of the iodide, or of the cyanide of a metal is united with one or more atoms of the oxide of the same metal. Turner's yellow, which is an oxychloride of lead ($PbCl$, 7 PbO), is a well-known commercial article belonging to this

class. Such combinations usually occur between oxides and chlorides or iodides of metals the pure chlorides or iodides of which never form any but anhydrous crystals, and which consequently cannot be supposed to take up an oxide as a substitute for water of crystallization: any satisfactory theory of the class of subsalts must also account for the formation of compounds of this kind. There is, indeed, much in the chemical nature of such compounds that requires further investigation.

Some salts enter into combination with other bodies, and form compounds which are in many respects anomalous; such for instance are the compounds of ammonia with many dry salts: 2 atoms of chloride of silver will in this manner absorb 3 atoms of ammonia. Many of the salts of copper exhibit a similar power (518).

CHAPTER XI.

GROUP I.—METALS OF THE ALKALIES.

§ I. POTASSIUM (K=39), *Sp. Gr.* 0·865.

Native Compounds which contain Potash.

Alum	$KO,SO_3 + Al_2O_3, 3\ SO_3 + 24\ Aq.$
Felspar	$(KNa)O, 3\ SiO_2 + Al_2O_3, 3\ SiO_2.$
Biaxal mica . . .	$KO, 3\ SiO_2 + 3[(AlFe)_2O_3,SiO_2]$

(464) *Symbols of Mixtures of Isomorphous Compounds.*—The formulæ employed above for felspar and mica require explanation, as the principle of notation adopted in these cases will be applied hereafter to the formulæ of a large number of minerals.

It often happens that isomorphous bases displace each other in the same mineral without altering its form or mineralogical characters, or even without altering its general chemical formula. Mica, for example, may be regard as a compound of 1 atom of a silicate of a protoxide of a metal with 3 atoms of a different silicate of a sesquioxide of a different metal. Let M stand for the metallic base of the protoxide, X for the metallic base of the sesquioxide; the general formula for mica may then be expressed thus:—

$$\text{Mica} = [MO, 3\ SiO_2 + 3\ (X_2O_3,SiO_2)].$$

Now the components of potash-mica are principally silicate of potash and silicate of alumina, the potash being the metallic protoxide and the alumina being the metallic sesquioxide; but sesquioxide of iron,

sesquioxide of manganese, and sesquioxide of chromium are also isomorphous with alumina; these compounds frequently displace a portion of the alumina from its combinations, and this is especially the case with the sesquioxide of iron. The peculiarity of isomorphous bases, when they displace each other, is this—that the displacement is liable to occur in any possible proportion; for example, in different specimens of mica the relative proportions of iron and aluminum are liable to great variations; this arises from the fact that the silicate of sesquioxide of iron and silicate of alumina, which are isomorphous, may be mixed in any conceivable proportion, and will crystallize together without altering the form of the mineral. The same fact may also be represented by stating that they may vary indefinitely in amount, provided only that the quantity of the two metals taken together in any one specimen furnishes such a proportion of a metallic sesquioxide as is equivalent to the silica in that portion of the mineral; that is to say, that the two proportionals of metal required for combination with the 3 proportionals of oxygen in the sesquioxide, may either consist wholly of aluminum, or a *small but indefinite* proportion of the aluminum may have its place supplied by a *small but equivalent* quantity of iron, or a large proportion of the aluminum may have its place supplied by a corresponding and equivalent proportion of iron.

Now the method of notation adopted in the preceding formulæ is employed to indicate precisely this—that the proportions of the two or more metals, the symbols of which are bracketed together, thus, $(AlFeMn)_2O_3$, are liable to vary within any conceivable limits, provided that the united amount of all the metals so bracketed be exactly sufficient to form a true sesquioxide with the three proportionals of oxygen.

In like manner, in the case of the potash in felspar, the place of part of the potassium may be supplied by sodium; but the proportions of the two taken together require exactly the same amount of oxygen, and consequently saturate the same proportion of silicic acid, that 1 equivalent of potash alone would have required.

This frequent partial displacement of one isomorphous base by another in native crystallized minerals, renders much caution necessary in interpreting the results of an analysis. The difficulty of fixing the formula of a mineral of course increases with the complexity of its composition, and it is with the silicates especially that these difficulties are experienced. It is usual, when the analytical operations are completed, to ascertain the proportion of

oxygen in the silicic acid, then the proportion of oxygen contained in the sesquioxides, and lastly the quantity of oxygen in the protoxides; because, however much the proportions of the different metals may vary in different specimens of the same mineral, the ratio of the oxygen in both sets of bases to the oxygen in the silicic acid remains uniform. In felspar, for instance, if the proportion of oxygen in the silicic acid be taken as 12, that in the sesquioxide of aluminum is 3, and that in the protoxide of potassium or sodium is 1.

(465) Potassium.—This remarkable metal was discovered by Davy, in the year 1807, and its isolation marks an important era in the progress of philosophical chemistry. The alkalies and the earths had long been suspected to be compound bodies, but up to that period they had resisted all attempts to decompose them. When once potassium, however, had been separated from its compounds, and potash had been proved to be an oxide of this metal, the decomposition of the other alkalies and earths followed as a necessary consequence: more correct ideas upon fundamental points of chemical theory were introduced; new methods of research were placed within reach of the analytical chemist, and potassium itself, from its powerful affinity for oxygen, became an important addition to the reagents of the laboratory.

Properties.—Potassium is a bluish-white metal, which is brittle, and has a crystalline fracture at 32°; at temperatures a little above this it is malleable; at 60° it is soft; as the temperature rises it becomes pasty, and at 130° it is completely liquid. Whilst in the soft condition, two clean surfaces of the metal admit of being welded together like iron; at a red heat it may be distilled, and it yields a beautiful green vapour. Potassium is light enough to float in water, having a specific gravity of only 0·865. If exposed to the air, even for a few minutes only, it becomes covered with a film of oxide: when heated to its point of volatilization it bursts into flame, and burns with great violence. The powerful attraction of potassium for oxygen is seen on throwing the metal into water, in which case part of the water is immediately decomposed; its oxygen combines with the potassium and forms potash, while the escaping hydrogen carries with it a small portion of the volatilized metal, and taking fire from the heat evolved, burns with a beautiful rose-red flame; the metal melts and swims about rapidly upon the water, and finally disappears with an explosive burst of steam, as the globule of melted potash which is formed by its oxidation becomes sufficiently cool to come into contact with the water. Potassium decomposes nearly all gases which contain

oxygen, if it be heated in contact with them; and at a high temperature it will remove oxygen from almost all bodies into the constitution of which that element enters. It becomes necessary therefore to preserve the metal either in exhausted, hermetically sealed glass tubes, or under the surface of some liquid, like naphtha, which does not contain oxygen. At a heat short of redness potassium absorbs hydrogen and becomes converted into a greyish mass. It enters directly into combination with the halogens and with sulphur, selenium, and tellurium, burning vividly when heated with them. It likewise absorbs carbonic oxide with facility when heated moderately in it, or when the vapour of potassium is allowed to condense slowly in an atmosphere of the gas; a black mass is thus formed from which the metal cannot be recovered, and which often occasions considerable waste in the ordinary method of preparing potassium.

(466) *Preparation.*—1. Davy originally obtained potassium by decomposing a fragment of hydrate of potash (which had become slightly moistened upon its surface by exposure to the air for a few minutes) by the current of a voltaic battery of 200 or 250 pairs of six-inch plates, on Wollaston's construction. The dry hydrate is an insulator, but a trace of moisture confers upon it a sufficient degree of conducting power: under such circumstances globules of metallic potassium are separated at the negative wire, and may be preserved under naphtha. They burn vividly in air, leaving an intensely alkaline residue. This method of procuring the metal, however, furnishes it only in very small quantity, and is difficult and expensive.

2.—Gay-Lussac and Thénard, in 1808, invented a method by which potassium may be obtained by purely chemical means in greater abundance. Iron turnings were heated to whiteness in a curved gun-barrel, which was covered with a clay lute, to preserve it from the action of the air at a high temperature, and melted hydrate of potash was allowed to pass slowly over the ignited iron; decomposition ensued, the iron combined with the oxygen both of the potash and of the water, and potassium along with hydrogen passed forwards, the potassium condensing in a copper receiver which was kept cool.

3.—The process by which potassium is now obtained consists in decomposing the carbonate of potash by charcoal, a plan originally invented by Curaudau, and improved by Brunner. This operation has been carefully studied by Donny and Mareska (*Ann. de Chimie*, III. xxxv. 144). In order to ensure a successful result, attention to a number of minute precautions is requisite.

The material which is best adapted to its preparation is the potash salt of some vegetable acid, which, when decomposed by heat in a vessel from which air is excluded, leaves a large quantity of carbon. For this purpose the acid tartrate of potash, or crude tartar, is preferred. About 6 lb. of this substance is placed in a capacious iron crucible furnished with a cover, and ignited till it ceases to emit combustible vapours. A porous mass of carbonate of potash, intimately mixed with very finely divided carbon, is thus obtained: this is rapidly cooled by moistening the exterior of the crucible with cold water; the charred mass, when cold, is broken up into lumps of about the size of a hazel-nut, and quickly introduced into a wrought-iron retort. This retort is usually made of one of the iron bottles in which mercury is imported; it is introduced into a furnace, *a*, as shown at *b*, fig. 310, and placed horizontally upon supports of fire-brick, *f f*; a wrought-iron tube, *d*, 4 inches

FIG. 310.

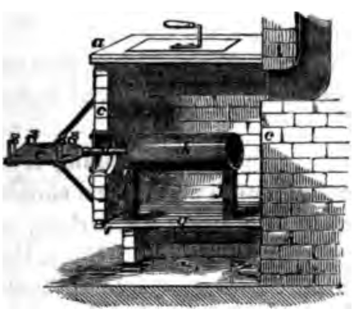
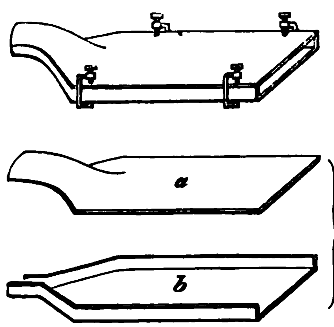


FIG. 311.



long, serves to convey the vapours of potassium produced during the distillation into a receiver, *e*, which it is found most advantageous to construct of the form shown separately in fig. 311. It consists of two pieces of wrought iron, *a*, *b*, which are fitted closely to each other, so as to form a shallow box only a quarter of an inch deep, and are confined in their places by clamp screws: the iron plate should be one-sixth of an inch thick, 12 inches long, and 5 inches wide; the receiver is open at both ends, the socket fitting upon the neck of the iron retort. The object of preparing the receiver of this particular form is to ensure the rapid cooling of the potassium, and so to withdraw it from the action of the carbonic oxide which is disengaged during the whole process. Before this receiver is connected with the tube, *d*, the fire is slowly raised until the retort attains a dull red heat; powdered vitrified borax is then sprinkled over its exterior; the borax melts, and forms a coating which protects the metal from oxidation. The

heat is then urged until it becomes very intense. A mixture of coke and charcoal forms a fuel well adapted to this purpose; care should be taken that the temperature of the furnace be raised as equally throughout every part as possible. When a full reddish-white heat is attained, vapours of potassium begin to appear, and burn with a brilliant flame: the receiver is now adjusted to the iron neck of the retort, which is not allowed to project more than a quarter of an inch through the iron plate which forms part of the front wall, *c*, of the furnace, lest the tube should become obstructed by the accumulation of solid potassium. Should any obstruction occur, it must be removed by thrusting in an iron rod; if this fails, the fire must be immediately withdrawn; this is readily effected by removing the fire bars, *g*, from the furnace, with the exception of two which support the retort; the fuel thus falls into the ashpit. The receiver is kept cool by the application of a wet cloth upon its exterior. When the operation is complete, the receiver with the potassium is removed, and instantly plunged into a vessel of rectified Persian naphtha, provided with a cover. The vessel is kept cool by immersion in water. When this apparatus is sufficiently cold, the potassium is detached, and preserved under naphtha.

In order to obtain the maximum produce of potassium, it is necessary that the mixture of carbonate of potash and carbon should contain 1 atom of carbonate of potash to 2 atoms of carbon, or 69 parts of the carbonate by weight to 12 of carbon. Upon the application of heat the mixture is wholly converted into carbonic oxide and potassium; $KO,CO_2 + 2\,C = K + 3\,CO$. The charge usually yields about one fourth of its weight of crude potassium, some loss during the process being inevitable. Donny and Mareska found this loss to amount to about one third of the entire quantity of the metal contained in the charge.

The potassium so obtained is not pure; it is necessary to subject it to a second distillation in an iron retort. This precaution is *essential;* for, if it be neglected, a black detonating compound is speedily formed by exposure to the atmosphere, and is even produced spontaneously, although the metal be kept under naphtha; this substance explodes violently upon the slightest friction. The purified metal amounts to about two thirds of the quantity operated on. A third distillation may be necessary if the potassium be required in a state of perfect purity. A little impure potassium almost always remains in the tube attached to the retort; and in order to prevent the possibility of the formation of the detonating

compound already mentioned, it is best to detach this tube as soon as it is cold, and to immerse it in water.

(467) OXIDES OF POTASSIUM.—Potassium forms two compounds with oxygen: a protoxide, which constitutes potash, the basis of the salts of the alkali; and a teroxide, which does not combine with acids.

		Potassium.		Oxygen.		
Potash	$KO = 47$	82·97	+	17·03	=	100
Teroxide of potassium	$KO_3 = 63$	61·90	+	38·10	=	100

Teroxide of Potassium ($KO_3=63$).—This substance is formed when potassium is burned in a silver spoon, or upon a mass of fused chloride of potassium in an excess of oxygen gas; a yellowish brown mass, fusible at a red heat, is thus obtained; as it cools, it assumes a scaly, crystalline texture. It parts readily with its excess of oxygen to combustibles, and is decomposed by water with extrication of oxygen and formation of a solution of pure potash, or protoxide of potassium.

(468) *Potash* ($KO=47$).—This compound can be procured in an anhydrous form by oxidating potassium in thin slices in air perfectly freed from moisture and carbonic acid. It is white, very deliquescent, and caustic; when moistened with water it becomes incandescent: after it has thus become hydrated, no degree of heat is sufficient to expel the water. Anhydrous potash fuses at a red heat, and is volatilized at a high temperature. For most purposes the presence of water is immaterial, potash is therefore generally procured in the state of hydrate, in which form it may be obtained without difficulty.

Hydrate of Potash, or *Caustic Potash* ($KO,HO=56$; *Sp. Gr.* 2·2) is prepared by dissolving carbonate of potash, of which the *pearlash* of commerce is an impure variety, in 10 or 12 times its weight of water, and adding to the boiling solution a quantity of caustic lime equal in weight to half the carbonate of potash used; the lime should be slaked, made into a thin paste with water, and added in small portions at a time, so that the liquid may be maintained at the boiling point: a crystalline carbonate of lime is precipitated, and hydrate of potash remains in solution; KO,CO_2+CaO,HO giving $KO,HO+CaO,CO_2$. After decantation from the precipitate the liquid is rapidly evaporated in a clean iron or silver basin, till, when the heat is raised nearly to redness, it flows without ebullition, like oil: it is then either cast into cylinders in a metallic mould, or is poured upon a cold stone slab, and solidifies on cooling. Hydrate of potash may be obtained

crystallized in acute rhombohedrons, ($HO,KO+4\ Aq$), from a hot concentrated aqueous solution.

Hydrate of potash is one of the most indispensable reagents to the chemist. It is therefore necessary that he should be able readily to ascertain its purity, and if needful prepare it for himself: when required, pure bicarbonate of potash, in crystals, may be decomposed in the manner above described by means of lime obtained from black marble. The impurities which occur most frequently in ordinary caustic potash are carbonic, sulphuric, hydrochloric, and silicic acids, lime, alumina, oxides of iron and lead, and teroxide of potassium. If pure, it is perfectly soluble in water without effervescence; a diluted solution gives no precipitate with baryta-water, showing the absence of carbonic and sulphuric acids; it yields no precipitate with oxalate of ammonia, showing the absence of lime. On neutralizing it with nitric acid, nitrate of silver gives no precipitate, showing the absence of chlorine. Freedom from iron or metallic impurities is shown by the absence of any precipitate on the addition of hydrosulphate of ammonia. Caustic potash, when pure, is wholly soluble in alcohol, the impurities above mentioned remaining undissolved. Common potash is therefore often purified by forming a solution of it in alcohol, and boiling down to dryness in a silver vessel, till it flows tranquilly; the alcohol is thus expelled, the melted hydrate is poured off upon a silver plate from the black crust which forms over its surface, and when cold it is broken up and placed in a well-closed bottle.

Wöhler obtains a solution of pure caustic potash by introducing into a crucible made of sheet copper a mixture of 1 part of pure nitre and from 2 to 3 parts of clean copper clippings; the mixture is then covered, and heated to moderate redness for about half an hour. The mass thus obtained is next treated with water, and the turbid solution allowed to deposit the oxide of copper in a tall narrow vessel, which can be closed; after which the clear liquid is drawn off.

A solution of pure potash may also be readily obtained by adding a hot solution of hydrate of baryta to a solution of sulphate of potash, until the liquid gives no further precipitate either with baryta or with the sulphate of potash; $KO,SO_3+BaO,HO= KO,HO+BaO,SO_3$.

Hydrate of potash, after fusion, is a hard, greyish-white substance: it rapidly absorbs both moisture and carbonic acid from the air; it is soluble in about half its weight of water, with the extrication of considerable heat; it is likewise soluble in alcohol to

an almost equal extent. Hydrate of potash has a peculiar nauseous odour, and an acrid taste; it is a powerful cautery, and quickly destroys both animal and vegetable matters; for this reason its solution cannot be filtered except through pounded glass or sand, and is always best clarified by allowing the impurities to subside, and then decanting the clear liquid. The solution should be preserved in glass bottles into the composition of which no oxide of lead enters, as the solution gradually dissolves this oxide out of the glass. It also attacks vessels even of green glass and of porcelain when heated in them.

The following table gives approximately the proportion of anhydrous potash contained in 100 parts by weight of solutions of the alkali of various densities:—

Strength of Solutions of Potash (*Dalton*).

Sp. gr.	KO in 100 parts.	Sp. gr.	KO in 100 parts.
1·60	46·7	1·33	26·3
1·52	42·9	1·28	23·4
1·47	39·6	1·23	19·5
1·44	36·8	1·19	16·2
1·42	34·4	1·15	13·0
1·39	32·4	1·11	9·5
1·36	29·4	1·06	4·7

The *Liquor Potassæ* of the pharmacopœia contains nearly 6 per cent. of the solid hydrate, and has a sp. gr. of 1·060. The concentrated solution used for organic analysis may be obtained by dissolving 1 part of the hydrate in 3 parts of water.

At a high temperature hydrate of potash is wholly volatilized; consequently the water cannot be expelled from this hydrate by the mere application of heat. Its affinities are so powerful that few vessels are found capable of resisting its action; those which contain silica are decomposed by it, and platinum itself is oxidized when heated in contact with it: gold and silver resist it better. Potash decomposes the fixed oils, and converts them into soluble soaps; when fused with siliceous minerals it displaces the bases, and combines with the silica, forming silicate of potash. Potash is extensively employed in the arts: to the soap-boiler and the glass-maker it is indispensable; when combined with nitric acid it enters largely into the manufacture of gunpowder, and in greater or less quantity it furnishes important aids to a variety of processes employed in the manufactures of the country. In the laboratory, potash is in constant use for absorbing acid gases such

as carbonic acid, and for separating the metallic oxides from solutions of their salts, since owing to the powerful affinity of the alkali for acids it readily decomposes the salts of all the metals which produce oxides insoluble in water.

Potash is present in small proportion in all fertile soils, the grand reservoirs of this alkali being the different varieties of clay, which contain 2 or 3 per cent. of it, derived from the disintegration of felspar, in which it exists in the proportion of from 10 to 12 per cent., and certain kinds of mica, which yield 5 or 6 per cent. By exposure to the air and atmospheric vicissitudes, these rocks become gradually disintegrated; their soluble constituents, potash amongst the number, are taken up by the water which falls upon the earth's surface, and are assimilated by the plants which spring from its bosom; they accumulate it, especially in the leaves, young shoots, and succulent parts. Owing to this circumstance large quantities of potash may be obtained with facility: dried brushwood is incinerated, and the remaining ash, which seldom constitutes more than 1 per cent. of the dry wood, contains the potash in the form of carbonate: the salt is extracted by water from the insoluble portions (479).

(469) SULPHIDES OF POTASSIUM.—Potassium takes fire readily and burns with brilliancy when heated in the vapour of sulphur. It combines with this element in not less than 4 and possibly in 5 different proportions, KS ?, KS_2,KS_3,KS_4, and KS_5. Owing to this circumstance, the reactions which occur when sulphur is heated with potash are somewhat complicated; but they are now well understood, and may be traced without difficulty.

Protosulphide of Potassium (KS).—Some doubt exists as to the possibility of forming this compound. The usual directions are to heat sulphate of potash in a current of dry hydrogen, or to mix sulphate of potash intimately with finely powdered charcoal, and ignite in covered vessels. Bauer, however, (*Chem. Gaz.* 1858, 468) finds that owing to the sulphuric acid being reduced before the alkali, the result is not that usually represented by the equation, $KO,SO_3+4\,H=KS+4HO$, but that a mixture of free alkali and a variable amount of one of the higher sulphides of potassium is the result. The residue obtained has a reddish-yellow colour; it is deliquescent, and acts powerfully upon the skin as a caustic. When a current of sulphuretted hydrogen is transmitted through a solution of caustic potash it is rapidly absorbed; and if the gas be allowed to pass till the liquid is completely saturated, the compound KS,HS, will be obtained in solution. It is colourless when first prepared, but if exposed to the

air quickly absorbs oxygen, and acquires a yellow colour, owing to the formation of bisulphide of potassium; $KS,HS+O=KS_2+HO$. It is usually stated that if a solution of potash be divided into two equal portions and one be converted into the hydrosulphate of sulphide of potassium (KS,HS), and be then mixed with the other half of the solution of potash, a solution of pure protosulphide will be obtained, $KS,HS+KO,HO$ becoming $2\,KS+2\,HO$. It is possible, however, that this is not so; but that both the caustic potash and the hydrosulphate remain unaltered in the liquid. On the addition of a stronger acid sulphuretted hydrogen is given off abundantly, and this would occur whichever view were correct, no sulphur being deposited; for $2\ KS+2\ (HO,SO_3)=2\,(KO,SO_3)+2\ HS$, and $KS,HS+KO,HO+2\ (HO,SO_3)=2\ (KO,SO_3)+2\ HS+2\ HO$.

If sulphate of potash be mixed in fine powder with half its weight of lampblack, and heated in a covered crucible, the sulphate is reduced to sulphide of potassium, which remains in a finely divided state mixed with the excess of charcoal, and yields a *pyrophorus*, or compound which takes fire spontaneously in the air, owing to the heat emitted by its rapid absorption of oxygen..

The *bisulphide* (KS_2) may be formed by exposing an alcoholic solution of KS,HS to the air till it begins to become turbid, and evaporating to dryness *in vacuo*. It fuses easily, and is of an orange colour.

The *tersulphide* (KS_3) is obtained pure by passing the vapour of bisulphide of carbon over ignited carbonate of potash as long as any gas makes its escape: carbonic acid and carbonic oxide are produced as follows; $2\ (KO,CO_2)+3\ CS_2=2\ KS_3+4\ CO+CO_2$. In the old process of making *liver of sulphur*, 69 parts of dry carbonate of potash are fused with 40 parts of sulphur; the resulting yellowish-brown mass consists of 3 atoms of tersulphide of potassium and 1 atom of sulphate of potash: part of the potash in this case yields oxygen to one portion of the sulphur, and forms sulphuric acid, as shown in the annexed equation: $4\ (KO,CO_2)+10\ S=(KO,SO_3+3\ KS_3)+4\ CO_2$.

A *tetrasulphide* (KS_4) may be formed by reducing sulphate of potash by the vapour of bisulphide of carbon.

The *pentasulphide* (KS_5) is formed by boiling a solution of any of the preceding sulphides with excess of sulphur till saturated, or by fusing any of the dry sulphides with an excess of sulphur; the exeess of sulphur separates and floats above the sulphide, which has a dark liver-brown colour; it is deliquescent, and forms a deep yellow solution in water.

All these sulphides have an alkaline reaction to test paper, and a more or less distinct odour of sulphuretted hydrogen. On the addition of a stronger acid they are decomposed with extrication of sulphuretted hydrogen, attended, in the case of all but the protosulphide, by the precipitation of white, finely divided sulphur. On adding the persulphide to an excess of hydrochloric acid of sp. gr. about 1·1, the persulphide of hydrogen (357) is separated as an oily liquid. By exposing solutions of the higher sulphides to air, they become colourless, hyposulphite of potash is formed, and the excess of sulphur is separated. When a solution of caustic potash is boiled with sulphur, a decomposition ensues similar to that which occurs when potash and sulphur are fused together; a deep reddish-yellow liquid is formed, which contains hyposulphite of potash, and one of the higher sulphides of the metal: 3 atoms of potash and 12 of sulphur would thus furnish 1 atom of hyposulphite and 2 of pentasulphide of potassium; $3(KO,HO) + 12\,S = KO,S_2O_2 + 2\,KS_5 + 3\,HO$.

(470) Chloride of Potassium ($KCl = 74·5$); *Sp. Gr.* 1·900. —This salt is extracted in considerable quantity from *kelp*, the ashes of burnt sea-weed, and is used largely as a source of potash in the manufacture of alum. It may be prepared pure by directly neutralizing bicarbonate or carbonate of potash with hydrochloric acid, and evaporating. It crystallizes in cubes, and is very readily soluble in cold water, which takes up about a third of its weight, attended with great depression of temperature. 100 parts of the salt contain 47·65 of chlorine and 52·35 of potassium. It is remarkable that this salt possesses the property of absorbing the vapours of sulphuric anhydride, forming a hard translucent mass ($KCl, 2\,SO_3$), which is instantly decomposed by water. With chromic acid it forms a corresponding compound ($KCl, 2\,CrO_3$), which is also decomposed by water: it is obtained in needles when a solution of bichromate of potash in hydrochloric acid is allowed to crystallize.

(471) Bromide of Potassium ($KBr = 119$); *Sp. Gr.* 2·672.— This is a very soluble salt, which crystallizes in cubes. 100 parts of it contain 67·22 of bromine and 32·78 of potassium. It may be obtained by adding bromine to a solution of caustic potash until the liquid acquires a slight permanent yellow colour: bromide of potassium and bromate of potash are formed. Löwig dissolves the mixed salts in water, decomposes the bromate by a current of sulphuretted hydrogen, warms gently to expel the excess of the gas, filters from the deposited sulphur, and evaporates till the solution crystallizes; $KO,BrO_5 + 6\,HS = KBr + 6\,HO + 6\,S$.

(472) Iodide of Potassium, or *Hydriodate of Potash* ($KI = 166$); *Sp. Gr.* 3·059.—This valuable medicine may be procured in several ways. A simple method consists in adding iodine to a solution of potash, gently warmed, until the solution begins to assume a brown tint. Iodide of potassium and iodate of potash are formed; $6\,I + 6\,KO = 5\,KI + KO,IO_5$. By gentle ignition of the residue obtained by evaporation, the iodate is decomposed, and the remaining iodide fuses. The salt must not be strongly heated, as iodide of potassium is volatilized by a red heat. A better plan is to digest 2 parts of iodine and 1 part of iron, in a stoppered vessel, with 10 parts of water, the iron being purposely added in excess; under these circumstances protiodide of iron is formed by the direct union of the metal with the iodine: the liquid is then boiled, and a solution of carbonate of potash is added in small quantities so long as a precipitate occurs; the solution is next filtered from the insoluble carbonate of iron, and on evaporation it yields crystals of iodide of potassium; $FeI + KO,CO_2 = KI + FeO,CO_2$.

Iodide of potassium crystallizes in anhydrous cubes, which in a dry air are not deliquescent. It is very soluble in water, and to a smaller extent in alcohol; it has a cooling, bitterish taste. 100 parts of this salt contain 76·5 of iodine and 23·5 of potassium. Its solution has the property of dissolving an additional equivalent of iodine, with which it forms a deep brown liquid.

Iodide of potassium, if pure, should be completely soluble in six times its weight of alcohol (sp. gr. 0·83); it should not effervesce when moistened with hydrochloric acid (carbonate of potash would be indicated by effervescence), and it should not turn brown by the action of the acid; if iodate of potash were mixed with it, free iodine would be shown by the brown colour developed on adding the acid.

Fluoride of Potassium ($KF = 58$) is a very deliquescent salt obtained by neutralizing hydrofluoric acid with a solution of potash. Its solution has an alkaline reaction and corrodes glass.

(473) Silicofluoride of Potassium ($KF,SiF_2 = 110$).—This salt is one of the most insoluble compounds of potassium; it falls as a transparent gelatinous precipitate whenever silicofluoric acid is added to a salt of potash; it dries to a white earthy-looking powder. Advantage is occasionally taken of its insolubility to separate potash from some of the acids with which it is united: in this way chloric acid is sometimes prepared from chlorate of potash.

(474) Sulphate of Potash ($KO,SO_3 = 87$); *Sp. Gr.* 2·64.—This salt contains 54·02 per cent. of acid, and 45·98 of potash. It crystallizes either in anhydrous six-sided prisms, terminating in

six-sided pyramids, or in four-sided oblique rhombic prisms; it requires about 16 parts of cold water for solution. The crystals decrepitate strongly when heated. Sulphate of potash forms a series of double salts with sulphates of the protoxides which are isomorphous with magnesia, and another class of salts (the varieties of alum) with the sulphates of the sesquioxides isomorphous with alumina. Jacquelain finds that if normal sulphate of potash be dissolved in nitric acid, a little nitre and bisulphate of potash are formed, whilst a salt consisting of $HO,NO_5 + 2\ (KO,SO_3)$, crystallizes in oblique prisms. An analogous compound may be formed with phosphoric acid, $3\ HO,PO_5 + 2\ (KO,SO_3)$.

Bisulphate of Potash, ($KO,HO, 2\ SO_3 = 136$); *Sp. Gr.* 2·475. —This salt is formed on a large scale as a residuary product in the preparation of nitric acid from nitrate of potash; it is the *sal enixum* of the older writers. It crystallizes from a strongly acid solution in rhomboidal tables, which fuse at a heat below redness, and by prolonged ignition lose half their acid; they are very soluble in water, and have a sour bitterish taste. If redissolved in water, the normal sulphate crystallizes first, and afterwards, when the liquid has become strongly acid, the bisulphate is deposited. The bisulphate occasionally crystallizes in anhydrous needles. This salt is sometimes used as a flux in cases where the action of an acid is required at a high temperature upon salts or metallic oxides with which it may be fused.

(475) Nitrate of Potash ($KO,NO_5 = 101$); *Sp. Gr.* 2·070.— *Saltpetre*, or *Nitre* as this salt is frequently termed, is one of the most important and valuable salts of potash. The principal supply of nitre is derived from various districts in the East Indies, where it occurs sometimes as an efflorescence upon the soil, at other times disseminated through the superficial stratum itself. It appears to be formed in the moist portions of the soil, at some little distance below the surface, towards which it is raised by capillary action. The nitre is obtained by lixiviating the soil, and allowing the solution to crystallize. The earth which furnishes it consists principally of loose, porous carbonate of lime, mixed with decomposing felspar, and it always contains more or less of organic matters. In temperate climates, both nitrites and nitrates are almost always found in the shallow well-waters of towns, owing to the oxidation of nitrogen contained in the animal debris during their infiltration through the soil. Notwithstanding the investigations of J. Davy, of Kuhlmann, and of others, the process of nitrification is still very imperfectly understood. The artificial formation of nitre has, however, been practised with considerable success in

various countries of Europe, which furnish annually a large amount of the salt. In Sweden, this supply of nitre is considered of such importance that each landed proprietor is obliged to pay a certain tax in raw nitre, the quantity required being proportioned to the value of the estate (Berzelius). Where animal matters are present in abundance, the formation of nitric acid is chiefly due to the gradual oxidation of ammonia developed in the process of putrefaction. The presence of a certain amount of moisture is necessary, and the oxidation is materially favoured by an excess of carbonate of potash, of lime, or of some basic substance which can combine with the acid at the moment of its generation. Ozone appears to have the power of combining directly with nitrogen; it may possibly, as Schönbein conjectures, be concerned in the natural production of nitric acid, and indeed it is not improbable that nitrification is, in favourable cases, due to the slow combination of atmospheric nitrogen and oxygen. The process of nitrification becomes arrested if the temperature be allowed to fall much below 60°.

Nitre Plantations.—The method adopted in the artificial production of nitre consists in placing animal matters, mingled with ashes and lime rubbish, in loosely aggregated heaps, exposed to the air, but sheltered from rain. The heaps are watered from time to time with urine or stable runnings; at suitable intervals the earth is lixiviated, and the salt crystallized. Three years usually elapse before the nitre bed is washed: after this interval a cubic foot of the *débris* should yield between 4 and 5 ounces of nitre. As there is always a considerable quantity of the nitrates of lime and magnesia present, which will not crystallize, carbonate of potash, in the shape of wood ashes, is added so long as any precipitate occurs. The nitrate of lime is decomposed, and the insoluble carbonate of lime separated; $KO,CO_2 + CaO,NO_5 = CaO,CO_2 + KO,NO_5$. The clear liquor is then evaporated and crystallized. It is found by the saltpetre-boiler that the earth in which nitre has once been formed furnishes fresh nitre more readily than on the first occasion. Care is taken that the *nitre plantations*, as they are termed, shall rest upon an impervious flooring of clay, so that the liquid which drains away from them may be collected and preserved.

In Prussia, by a more methodical treatment, a cubic foot of the earth yields about 20 ounces of nitre. The heaps are so constructed as to form a terrace of steps, exposing the back in the form of an upright wall to the prevailing wind; the watering is thus facilitated, while upon the exposed side the evaporation proceeds with rapidity, and here, from capillary action, the nitre

chiefly accumulates: from time to time a layer of earth is removed from this wall for lixiviation, and the washed earth, mixed with a fresh portion of animal matter, is returned systematically to the other side of the heap.

The washing of the earth charged with saltpetre is conducted in a systematic manner, so as to avoid using a larger quantity of water than is actually needed to dissolve the saltpetre. The operation resembles that employed in washing ball-soda (491), and is minutely described by Regnault (*Cours Elémentaire de Chimie*, ii. 131).

Besides the natural and artificial sources of nitre just described, this salt occurs also in solution in the sap of certain plants, among which the sunflower, the tobacco plant, and common borage may be enumerated.

Properties.—Nitre usually crystallizes in long six-sided striated prisms, terminated by dihedral summits; but it is a dimorphous salt, and is occasionally obtained by spontaneous evaporation of small drops of its solution in microscopic rhombohedra, isomorphous with those of nitrate of soda: it is soluble in $3\frac{1}{2}$ times its weight of cold water, and about a third of its weight of boiling water; it is insoluble in alcohol: its taste is cooling and saline. If paper be dipped in a solution of nitre and dried, it forms what is well known as *touch-paper*, which, when once kindled, steadily smoulders away till consumed, and hence it is largely employed in firing trains of powder, fireworks, &c. Nitre fuses easily without decomposition at a temperature of 642°, and when cast into moulds, solidifies to a white, fibrous, translucent, radiated mass, known as *sal prunelle.* When heated to redness, part of its oxygen is expelled, and a deliquescent mass of nitrite of potash is formed. By a still stronger heat the nitrite is decomposed, nitrogen mixed with oxygen escapes, and a mixture of potash and teroxide of potassium remains. 100 parts of nitre contain 53·46 of nitric acid and 46·54 of potash.

Owing to the facility with which nitre parts with oxygen, it is a powerful oxidating agent, and is in frequent demand in the laboratory for this purpose: when thrown upon glowing coals it produces a brisk scintillation. If nitre be intimately mixed with any metallic sulphide in fine powder, such as sulphide of antimony, and thrown in small quantities at a time, into a red-hot crucible, the sulphur burns with a brisk *deflagration,* or rapid combustion, into sulphuric acid, which combines with the potash of the nitre, whilst the metal at the same time becomes oxidized to the maximum. In the case of antimony, the oxide produced possesses acid

ɜrs, and it enters into combination with the potash. Ad- is frequently taken of this oxidizing action of nitre in order ert small quantities of sulphur in bodies of organic origin phuric acid, for the purpose of estimating the proportion hur which they contain. The quantity of sulphuric acid ɔduced, admits of easy and accurate determination in the sulphate of baryta.

5) *Refining of Saltpetre.*—The impurities of most frequent nce in nitre are sulphate of potash, chlorides of potassium and and nitrates of lime and magnesia: after it has been fused, the heat has been cautiously regulated, a little nitrite of is liable to be formed; in the latter case a fragment of the en moistened with solution of sulphate of copper, becomes of t green colour. Nitre may be quickly deprived of chlorine stening the powdered salt with pure nitric acid and gently it, until a portion of it when dissolved in water, gives no ate with nitrate of silver. Nitre, when pure, is not deli- t, and its solution gives no precipitate with solutions of of barium, of nitrate of silver, or of carbonate of potash.

;he refining of nitre advantage is taken of the circumstance ilst the solubility of nitrate of potash rapidly increases as perature rises, that of the chloride of sodium is scarcely by it. It was formerly the practice to purify the salt by ccessive crystallizations; but the same object is now effected gle operation, in the following manner:—In a deep copper ıbout 50 gallons, or 500 lb. of water is placed, and twice ht of crude nitre is added: this salt gradually becomes l, and fresh nitre is added until, when the water has attained ing point, a quantity of nitre has been added equal to three ıe weight of the water employed;* when the liquid has ıdered clear by a few minutes' ebullition, it is strained bag filters, and allowed to run into the crystallizing pan. crystallization is effected in a shallow vessel, the bottom of formed by two inclined planes which meet in the middle.

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quantity of chloride of sodium in East Indian nitre is generally .t in the artificial nitre obtained from the 'beds' it often rises to a unt: in such a case the liquid is skimmed from time to time, and de of sodium, a large proportion of which remains undissolved, is by means of perforated ladles; as soon as nitre equal to about 5 weight of the water has been added, the solution is diluted with twice ity of water at first employed, after which, if the liquid be strongly 2½ lb. of glue, dissolved in hot water, are added, and thoroughly in- l by briskly stirring; the coagulum which is formed rises in a the surface, collecting the whole of the organic impurities derived nitre heap; this is carefully removed, and the operation is after- .tinued as above described.

In this vessel the solution is kept in continual agitation, in order to prevent the formation of large crystals: such crystals would mechanically retain the mother-liquor, from which they could not be subsequently freed without recrystallization. The chloride of sodium, being nearly as soluble in cold water as in hot, remains almost entirely in the solution, whilst the saltpetre is deposited in extremely small crystals, technically termed *saltpetre flour;* these are allowed to drain, and are then removed to tanks provided with false perforated bottoms, where they are deprived of the mother-liquor with which they are saturated. For this purpose the tanks are completely filled with the crystals, and upon them is poured a solution of saltpetre saturated in the cold; this liquid dissolves the chlorides, but leaves the pure nitrate of potash undissolved. In the course of a few hours the liquid is drawn off, and the tanks are then filled up with pure water; this becomes charged with nitre containing traces of chlorides, whilst the undissolved salt is almost chemically pure: the solution of nitre thus obtained serves to wash a fresh portion of the crystals: the refined saltpetre is then dried, and is fit for use.

(477) *Gunpowder.*—The principal consumption of nitre is in the manufacture of gunpowder, which consists of an intimate mechanical mixture of nitre, sulphur, and charcoal, in proportions approaching to 1 atom each of nitre and of sulphur, and 3 atoms of charcoal:—

			In 100 parts.
Nitre	KO,NO_5	$=101$	74·8
Sulphur	S	$=16$	13·3
Charcoal	C_3	$=18$	11·9
		135	100·0

The proportions used vary a little in different countries, as will be seen from the following table:—

Composition of Gunpowder in 100 *parts.*

	English and Austrian.	Prussian.	Swedish.	Chinese.	French.		
Nitre	75	75·	75	75·7	75·0	76·9	62
Sulphur	10	11·5	9	9·9	12·5	9·6	20
Charcoal	15	13·5	16	14·4	12·5	13·5	18
	Musket.	Musket.	Musket.		Musket.	Sporting.	Blasting.

An excess of sulphur is carefully avoided, on account of its injurious action upon the metal of the gun. The great explosive power of gunpowder is due to the sudden development of a large volume of nitrogen and carbonic acid gases, which, at the ordinary

temperature of the air, would occupy a space equal to about 300 times the bulk of the powder used; but from the intense heat developed at the moment of the explosion, the dilatation amounts to at least 1500 times the volume of the gunpowder employed. Supposing the mixture to be made in the proportion of 1 atom of sulphur, 1 of nitre, and 3 atoms of carbon, the reaction may be approximatively represented thus:—

$$S + C_3 + KO,NO_5 = (3\ CO_2 + N) + KS.$$

The only solid residue therefore is sulphide of potassium, and part of this also is volatilized by the heat of the explosion, burning, and forming the white smoke; it is this substance which gives the peculiar sulphurous odour to the washings of a gun-barrel.*

Much care is requisite in the selection of the materials for the manufacture of gunpowder. The charcoal must be burned thoroughly, but not at too high a temperature: that from the willow, alder, or dogwood is preferred for the purpose, dogwood charcoal being employed only in making rifle powder. In the government works at Waltham Abbey, sulphur is never used in the state of flowers of sulphur; in this condition it is preferred for fireworks; but distilled sulphur, reduced to a fine meal by grinding, is always used for gunpowder. The flowers of sulphur always contain sulphurous acid, which becomes speedily converted into sulphuric acid and attracts moisture. Nitre of the purest quality is alone employed. These three materials having been separately ground and sifted, are mixed in powder in the proper proportions, and are intimately blended in a revolving drum; they are then made into a stiff paste with water, and ground for some hours under edge-stones in the *incorporating mill;* the slightly coherent mass thus procured is broken up, and spread, in layers of about an inch in thickness, between gun-metal plates; it is then subjected to the action of a hydraulic press which exerts a force of 70 tons upon the square foot: a hard, sonorous mass, termed *press cake,* is thus obtained: these masses, whilst still damp, are broken into small fragments, or *granulated,* by submitting them to the action of toothed rollers in a machine constructed for the purpose. The grains are next sorted by means of sieves into different sizes, after which they are

* In burning gunpowder in a copper tube with the view of collecting the gases over mercury, Chevreul found a small proportion of deutoxide of nitrogen, of carbonic oxide, and of carburetted hydrogen, with a little sulphuretted hydrogen, mixed with the nitrogen and carbonic acid. Bunsen, and Linck, obtained results somewhat different, but the temperature, and consequently also the results of the combustion procured by this regulated action, are very different from those attending the firing of ordnance.

thoroughly dried in closets heated by steam, and, finally, are *glazed*, or polished by placing them in barrels caused to revolve about 39 times in a minute. Mining powder is often glazed by adding powdered graphite in the polishing barrels; this operation retards the rate of ignition, and diminishes the hygroscopic character of the powder. A cubic foot of good English cannon powder weighs about 58 lb.; if below 55 lb., it is considered unfit for use. The heavier the powder the greater is its explosive power. Two ounces of the best English powder, when introduced into a mortar of 8 inches diameter, set at an angle of 45°, should throw a 68lb. shot from 260 to 280 feet, on level ground.

Good gunpowder burns rapidly in the open air, leaving little residue, not blackening or kindling paper upon which it is fired. It has been found that a powerful concussion of powder between two pieces of iron will frequently kindle it, and if the powder be placed upon lead, or even upon a board, it may be exploded by the blow of a leaden bullet fired at it.

The object of granulating the powder, independently of its diminishing its tendency to absorb moisture, is to favour the rapidity of inflammation, by leaving interstices through which the flame is enabled to penetrate and envelope each grain. The ignition of the whole charge does not take place simultaneously throughout, nor is it desirable that it should do so, otherwise sufficient time would not be given to allow the ball to receive the full advantage of the expansive force of the air generated: too rapid an action would be expended upon the barrel of the gun itself, and effects would be produced like those due to fulminating mercury; where a prolonged heaving force is required, as in blasting for mining operations, the action of the powder is still further retarded by mixing it with sawdust; the powder for this purpose usually contains 65 parts of nitre, 20 of sulphur, and 15 of charcoal. In the formation of the fusee, the quick and slow match, and certain kinds of fireworks, gunpowder is mingled with combustibles in various proportions.

The analysis of gunpowder is easily effected: 100 grains of the powder for examination are dried over sulphuric acid *in vacuo;* the loss indicates the amount of moisture. The residue is digested in water, and washed: the solution, when evaporated in a counterpoised capsule, and weighed, furnishes the amount of nitre, and other salts. Nitrate of baryta, when added to a solution of these salts, acidulated with nitric acid, will yield the sulphuric acid in the form of sulphate of baryta; and nitrate of silver, when added to the liquid filtered from the sulphate of baryta, will give

the data for ascertaining the amount of chlorine from the precipitated chloride of silver. The charcoal and sulphur are contained in the portion which did not dissolve in water; they may be separated by means of bisulphide of carbon, or by the use of benzol at a boiling temperature, which dissolves out the sulphur, and leaves it in the crystalline form by spontaneous evaporation, whilst the charcoal is left undissolved and may be weighed.

A mixture of 3 parts of nitre, 2 of carbonate of potash, and 1 part of sulphur, produces a compound known as *pulvis fulminans*, which when heated on an iron shovel until fusion takes place, suddenly explodes with a very loud report.

NITRITE OF POTASH (KO,NO_3) is a white, anhydrous, deliquescent salt, which may be obtained in crystals. It may be procured by decomposing nitre by fusion at a red heat, dissolving the residue in water, and allowing the nitre to crystallize out of the deliquescent nitrite, which may be obtained by evaporating the solution to dryness.

(478) CHLORATE OF POTASH ($KO,ClO_5=122{\cdot}5$); *Sp. Gr.* 1·989.—One mode of preparing this salt has already been explained (321). It may be more economically obtained by exposing to a current of chlorine gas a mixture, in a slightly damp state, of 69 parts of carbonate of potash and 168 parts of caustic lime, previously reduced to the state of hydrate; chlorate of potash, carbonate of lime, and chloride of calcium are formed: boiling water dissolves both the chlorate of potash and the chloride of calcium. The two salts are easily separated by crystallization, as the chlorate requires 16 parts of cold water for solution, and the chloride is soluble to almost any extent. The chlorate of potash is deposited in anhydrous, rhomboidal, pearly tables; it has a cooling taste, somewhat analogous to that of nitre: 100 parts of boiling water dissolve 61·5 of the salt. When heated to between 700° and 800° the salt melts, and at a higher temperature is decomposed, furnishing oxygen gas of great purity, and leaving chloride of potassium as a fixed residue behind. 100 parts of the salt contain 61·64 of chloric acid, and 38·36 of potash: when heated to redness, 60·21 parts of chloride of potassium are left, and 39·79 of oxygen evolved. The chlorate is a more powerful oxidizing agent than nitrate of potash; and if combustible substances, such as sulphur or phosphorus, be rubbed with it forcibly, combination with oxygen, accompanied by detonation, ensues. Chlorate of potash is principally consumed in the manufacture of lucifer matches, and as an oxidizing agent in certain operations of the

calico printer. When added to a solution acidulated with hydrochloric acid, it is often used in the laboratory as an oxidizing agent.

The friction tubes employed for firing cannon are charged with a mixture of 2 parts of chlorate of potash, 2 of sulphide of antimony, and 1 part of powdered glass. A mixture known under the name of *white gunpowder*, consisting of chlorate of potash, dried ferrocyanide of potassium, and sugar, has sometimes been manufactured for blasting purposes; but its preparation is attended with very great danger, owing to the facility with which it explodes by friction, a circumstance which has caused several fatal accidents.

PERCHLORATE OF POTASH ($KO,ClO_7 = 138{\cdot}5$) crystallizes in anhydrous, prismatic needles, which are very sparingly soluble in cold water; its principal properties and the mode of preparing it have been already described (322). 100 parts of the salt contain 66·07 of perchloric acid, and 33·93 of potash; when heated to redness it gives off 46·11 per cent. of oxygen, leaving 53·89 of chloride of potassium.

(479) CARBONATE OF POTASH ($KO,CO_2 = 69$); *Sp. Gr.* 2·103. —This important salt is obtained in large quantities for commercial purposes by lixiviating wood ashes, and evaporating the solution until it crystallizes; the mother-liquor, when it cools, is poured off from the crystallized salts, as it retains the more soluble carbonate of potash, and when evaporated to dryness, affords the *potashes* of commerce, and these, when calcined, yield the impure carbonate known as *pearlash*. Different plants, when burned, furnish varying quantities of the alkali, which they extract from the soil: the leaves and young shoots, where the vital action is the most vigorous, are the parts which furnish the greatest quantity of alkali. Herbaceous plants, therefore, generally furnish more than shrubs, and shrubs more than an equal weight of timber. It appears from the experiments of Violette that the variation in the quantity of ash obtained from different parts of the same tree is extremely great. Thus, taking the quantity of ash found in the heartwood as the unit of comparison, the proportion in other parts was as follows:—

Heartwood	1	Bark of branches	11
Root bark	5	Root fibres	16
Bark of trunk	9	Leaves	25

and it is stated by Chevandier (*Ann. de Chimie*, III. x. 129) that

he quantity of ash varied as follows for 100 parts of different ortions of the wood of the undermentioned trees:—

	Solid stem.	Arms.	Small branches.
Beech	0·73	1·54	0·72
Oak	1·94	1·49	1·32
Birch	0·57	1·00	0·48

In the wine-producing countries, a considerable quantity of arbonate of potash of good quality is furnished by burning the efuse yeast after the fermentation is complete. The yeast, for his purpose, is pressed, dried in the sun, and burned in shallow nclosures: this dry yeast furnishes nearly 10 per cent. of its eight of the carbonate. Potash does not exist in plants in the orm of carbonate; it occurs in them in union with different rganic acids: these organic acids are destroyed by the action of he heat during incineration. These acids always contain more arbon than is sufficient, when oxidized by the air, to form the mount of carbonic acid requisite to neutralize the potash; and he carbonate of potash thus produced, as it is not decomposed by red heat, remains behind. In the ashes of plants various other aline substances are likewise present, but those which are soluble onsist principally of the sulphate of potash and chloride of otassium; these alkaline salts usually amounting to from 10 to o per cent. of the entire quantity of ash.

A purer carbonate is obtained for chemical purposes by deflagrating a mixture of purified cream of tartar with an equal quanity of pure nitre. The mass is thrown, in small portions at a ime, into a red-hot crucible: in this operation the nitre yields oxygen to the vegetable acid, converting the carbon which it contains into carbonic acid, which enters into combination with the alkali both of the tartar and of the nitre, since the two acids undergo mutual decomposition: the carbonate of potash is extracted from the dry mass by lixiviation.

Carbonate of potash is a deliquescent salt, which is with difficulty obtained in oblique rhombic octohedral crystals with 2 Aq. 100 parts of the anhydrous salt contain 68·11 of potash, and 31·89 of carbonic acid. Its reaction upon test paper is strongly alkaline; it has an acrid, alkaline taste. Its solutions have a peculiar lixivial smell: 100 parts of water at 60° dissolve 90 of carbonate of potash; and at the boiling point take up 205 parts, or rather more than twice their weight, of the salt. Alcohol does not dissolve it. Carbonate of potash fuses by exposure to a red heat, and at a very high temperature is partially volatilized; at a red heat it is decomposed by silica, carbonic acid being expelled with effervescence, whilst the silica, uniting with the alkali, forms with

it a true silicate, the basis of one of the varieties of glass. Advantage is taken of this property in the analysis of mineral substances which contain a large quantity of silica, and which are not easily decomposed by the action of acids. For this purpose the mineral to be analysed is reduced to an extremely fine powder by careful levigation; a portion of this powder is accurately weighed, and then intimately mixed with about 3 times its weight of carbonate of potash (or, still better, with thrice its weight of a mixture of $5\frac{1}{2}$ parts of dried carbonate of soda and 7 parts of carbonate of potash); the whole is introduced into a platinum crucible, and exposed to a bright red heat for an hour. The mass enters into fusion, carbonic acid escapes with effervescence, and a silicate of potash is formed, by which means all the bases of the mineral, which before were combined with the silica, are set at liberty. Upon now treating the mass with diluted hydrochloric acid, the silicate of potash is decomposed, the earths and metallic oxides are dissolved, and the silica is partially dissolved and partially separated in the hydrated form. In order to decompose the hydrate of silica, the solution is evaporated to dryness, moistened with hydrochloric acid, and again treated with water; the whole is now placed upon a filter, and the silica, after being well washed, remains behind in a state of purity. The analysis of the filtered liquid is then finished according to the ordinary method adopted for substances directly soluble in acids.

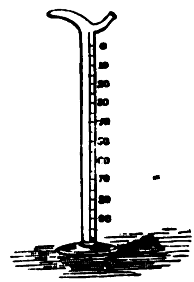
Carbonate of potash is largely consumed in the arts, as for example, in the manufacture of soap and of glass, and for preparing caustic potash and other compounds of potash. It also furnishes the chemist with one of his most indispensable reagents.

(480) *Alkalimetry.*—Since the quantity of alkaline carbonate is liable to great variations in different samples of the ash; and since the commercial value of pearlash depends upon the amount of carbonate which it contains, a rapid and sufficiently accurate method of analysis of this salt becomes a desideratum. In order to effect this object, the process termed alkalimetry has been invented. In principle it depends upon the determination of the number of divisions of a diluted acid, of definite strength, which 100 grains of the different samples of ash are capable of neutralizing; the neutralization being estimated by the action of the solution upon blue litmus paper.

The acid solution which is to be employed is measured from a burette or *alkalimeter*, which is a tube of the form shown in fig. 312. It has an internal diameter of about five-eighths of an inch, and is sufficiently tall to contain rather more than 1000 grains of

distilled water. The space occupied by 1000 grains of water at 60° is marked off and indicated as 0, and the tube is then subdivided into 100 equal parts, each capable of containing 10 grains of water: opposite every tenth division the number corresponding to it is placed, the numbers increasing from above downwards.

FIG. 312.



Various plans have been proposed for preparing the diluted acid; the following is substantially the same as that recommended by Faraday (*Chemical Manipulation*, 3rd ed., p. 281). It has the advantage of being readily applicable to any alkali.

A solution of sulphuric acid is prepared by diluting the ordinary commercial acid with 8 times its *bulk*, or nearly 5 times its weight of distilled water; when cool, the liquid, which may be termed *alkalimetric acid*, should have a specific gravity of 1·1268. In order to ascertain whether the strength of this alkalimetric acid be accurately adjusted, a quantity of crystallized bicarbonate of potash is fused in a platinum crucible in order to convert it into the carbonate: the fused mass is poured upon a clean iron plate, and 100 grains of it are quickly weighed, and dissolved in about 3 ounces of water in a small evaporating basin. Diluted acid, sufficient to fill 35 divisions, is now to be introduced into the alkalimeter, which consequently is to be filled up to the mark 65 with the diluted acid, and water is to be added until it stands at the mark 0: the acid and water are to be thoroughly mixed by closing the tube with the thumb and finger, then inverting and agitating the tube; after which the liquid is added to the solution of carbonate of potash, which is to be gently warmed in order to expel the carbonic acid as it is liberated. A piece of blue litmus paper, or a small quantity of infusion of litmus, is placed in the basin, and the acid is cautiously added until the litmus is distinctly but permanently reddened. The acid liquid, if properly diluted, ought to contain, in each division, sufficient sulphuric acid to neutralize 1 grain of carbonate of potash; and the entire contents of the alkalimeter should, therefore, exactly produce this effect. If more than 100 divisions of the acid be required, the test acid is too weak; if less than 100 divisions, it is too strong.

Suppose that 95 divisions of the acid were sufficient, the alkalimetric acid from which it was prepared must have contained one twentieth too much acid; every 95 measures of this acid, therefore, must be diluted with 5 measures of water. If, on the

other hand, more acid than 100 divisions be required, say 105 be needed, the acid contains one twentieth too much water; the quantity of alkalimetric acid used in the experiment requires the addition of one twentieth more of acid than it originally contained; now the quantity of alkalimetric acid used was 35 divisions, and the one twentieth part of this is 1·75, but only one fifth of this is pure acid (HO,SO_3), so that 0·25 parts by *weight* of the oil of vitriol originally used, must be added to each 35 parts by weight of alkalimetric acid. This correction, though not mathematically exact, is perfectly sufficient for all practical purposes. The alkalimetric acid, when duly adjusted, is preserved in bottles which are accurately closed.

Having thus prepared a test acid of the proper strength, 100 grains of the sample of pearlash for trial are dissolved in 3 or 4 ounces of water, filtered if necessary, and then tested in the same manner: the number of divisions of acid consumed will indicate the per-centage of carbonate of potash present in the sample.

The same acid may be employed to determine the quantity of soda present in any sample of soda ash; but as a certain weight of soda neutralizes a proportionately larger amount of acid than an equal weight of potash, the alkalimeter must be filled to a higher mark with the acid. For the determination of the quantity of pure potash in any sample, the acid must be poured into the burette till it stands at the division 49, and the tube must be then filled up to 0 with water. Each division will then contain acid sufficient to neutralize 1 grain of anhydrous potash.

If filled with acid to 65, and then filled up with water, each division will correspond to 1 grain of carbonate of potash.

If filled to 54·6, and then filled up with water, each division will indicate 1 grain of dry carbonate of soda: and if filled to 23·4, and then water be added to 0, the acid in each division will neutralize 1 grain of anhydrous soda.

In cases where greater accuracy is required, the acid solution, instead of being measured from the burette, is weighed; and for this purpose the solution is placed in a light flask of the form shown in par. (796).

In estimating the value of soda ash, which often contains sulphide of sodium and hyposulphite of soda, an error might be occasioned by adopting this method; because both the sulphide of sodium and the hyposulphite of soda would be decomposed by the sulphuric acid, and would neutralize it, and thus would be reckoned as carbonate of soda.

The presence of caustic alkali in any sample is easily ascer-

tained by the action of the solution upon nitrate of silver: the carbonates of the alkalies occasion a white precipitate of carbonate of silver; but if they contain any caustic alkali, a brown precipitate of hydrated oxide of silver is produced. The presence of sulphides in the ash is immediately manifested by the odour of sulphuretted hydrogen which is evolved on neutralizing the solution with an acid; if any sulphide be present, it will blacken the salts of silver, and interfere with their application as a test for caustic potash or soda.

FIG. 313.

(481) *Alkalimetry; Process of Will and Fresenius.*—The proportion of carbonic acid in any sample of alkali is readily ascertained by means of the apparatus employed for the purpose by Will and Fresenius, represented in fig. 313: *b* is a light flask, of about 3 ounces capacity, in which 100 grains of the alkali are placed with about 1 ounce of water: *d* is a similar flask, in which about an ounce and a half by measure of oil of vitriol is placed. A sound cork is fitted into the neck of each flask, and is pierced with two apertures for the reception of the tubes, *a*, *c*, and *e*, all of which are open at both ends: the tube, *a*, is sufficiently long to dip into the liquid in the flask; *c* is a bent tube, the longer limb of which passes into the acid in the flask, *d*. The outer extremity of *a* is closed during the experiment, by a plug of wax or of soft cement. The apparatus is charged in the manner already described, and is accurately weighed after it has been connected together. A partial vacuum is now made by applying the mouth to the tube, *e*, and exhausting a portion of the air; on ceasing to exhaust, the acid rises in the tube, *c*, and passes over into *b* to supply the place of the air which has been withdrawn; effervescence is occasioned by the escape of the carbonic acid, which passes off through the tube, *c*, and is dried as it bubbles up through the oil of vitriol in the flask, *d*. As soon as the effervescence has ceased, a fresh portion of acid is forced over from *d* into *b* by again partially exhausting the air: and this process is repeated until no further effervescence is occasioned by the fresh acid. The plug of wax is now withdrawn from the tube *a*, and a current of air is forced through the apparatus by exhausting with the mouth at *e*, and the carbonic acid is thus completely displaced. The plug is now replaced in the tube *a*, and the apparatus is weighed a second time. The difference between this weight and that obtained on

the first occasion, indicates the amount of carbonic acid which has been expelled.

If any sulphide or sulphite of the alkali be present, the error which it might occasion by loss of sulphuretted hydrogen, or of sulphurous acid, in the gaseous state, and which would be reckoned as carbonic acid, is prevented by mixing from 20 to 30 grains of neutral chromate of potash with the sample under trial: the chromic acid which is liberated by the subsequent action of the sulphuric acid upon the chromate, imparts oxygen to the sulphuretted hydrogen or sulphurous acid, and converts both into sulphuric acid, which would be retained, and would in no way interfere with the result.

(482) *Bicarbonate of Potash* ($HO,KO,2CO_2=100$); *Sp. Gr.* 2·052.—By passing a current of carbonic acid through a strong solution of the carbonate of potash, crystals of the bicarbonate are deposited in the form of right rhombic prisms; they are permanent in the air, and require about 4 parts of cold water for solution. The solution of the bicarbonate, if exposed to the atmosphere, gradually loses one fourth of its carbonic acid, forming a sesquicarbonate; and if boiled, the same change occurs much more quickly. The bicarbonate is converted into the neutral carbonate when fused by means of heat. The bicarbonate of potash has no alkaline reaction upon turmeric. It may be employed for procuring the compounds of potash in great purity, since, if well crystallized, it is almost absolutely pure, and may be obtained in this state with less difficulty than any other salt of potash. It is consumed medicinally in considerable quantities, for making effervescing draughts by the addition of citric or tartaric acid to its solution in water.

The *Silicates of Potash* are important compounds in connexion with the manufacture of glass; they will be noticed in treating this subject (495 *et seq.*).

(483) CHARACTERS OF THE SALTS OF POTASSIUM.—The salts of potassium, with a colourless acid, are all colourless. They seldom contain any water of crystallization, yet many of them are deliquescent: the carbonate and acetate offer striking instances of this peculiarity, and furnish in this respect a marked contrast to the corresponding salts of sodium. The salts of potassium, when pure, if introduced upon a platinum wire into the *reducing flame of the blowpipe*, communicate to it a violet tint; the presence, however, of a small quantity of a salt of sodium masks this effect, in consequence of the strong yellow flame occasioned in similar circum-

stances by the compounds of soda. Solutions of the salts of potassium yield no precipitate with solutions of the carbonates of the alkalies, with ferrocyanide of potassium, or with hydrosulphate of ammonia. The presence of potassium in solution is recognised, after the absence of every metal but sodium has been ascertained by the following characters :—1. If moderately concentrated, a solution of *tartaric acid* in excess causes, upon brisk stirring, a white crystalline precipitate of bitartrate of potash, which is readily dissolved upon adding an alkali. 2 and 3.—*Perchlorate* or *Carbazotate* of soda has also sometimes been employed as a test for potash, since both the perchloric and carbazotic acids form potassium salts of sparing solubility. These compounds, however, are all soluble to a considerable extent in cold water, and unless tolerably strong solutions are employed, they do not immediately subside. 4.—With *silicofluoric acid* they yield a transparent gelatinous silicofluoride, which forms a white powder on drying. 5.—The most conclusive reaction, however, is produced with the *bichloride of platinum*; upon mixing a strong solution of this salt with a concentrated one of a salt of potassium, a yellow double salt, consisting of ($KCl,PtCl_2$) is separated in crystals; it is quite insoluble in alcohol and ether, but is slightly taken up by cold water. It is therefore best for analytical purposes to acidulate the solution suspected to contain potassium with a little hydrochloric acid, and having added a slight excess of the solution of bichloride of platinum, to evaporate to dryness over the water bath, and to wash the residue with alcohol so long as anything is dissolved. This salt when heated to redness is decomposed, the platinum loses its chlorine, and the chloride of potassium may be dissolved out of the grey residue with cold water, whilst metallic platinum is left behind. 100 parts of the chloride of platinum and potassium are equivalent to 15·98 of potassium, or to 19·26 of potash.

§ II. Sodium (Na=23); *Sp. Gr.* 0·972.

(484) Sodium may be obtained from carbonate of soda by a process analogous to that used for potassium. Deville recommends the employment of the following mixture in the preparation of sodium :—

Dried carbonate of soda	. . . .	717 parts.
Powdered charcoal	. . . . . .	175 „
Finely powdered chalk	. . . .	108 „

These materials are mixed intimately and kneaded into a stiff paste with oil, and calcined in a covered iron pot: the mass is then

introduced into an iron retort and distilled, with the precautions described when speaking of potassium; it ought to yield nearly one third of its weight of sodium: the object of adding the chalk is to prevent the charcoal from separating from the carbonate of soda when this salt fuses. As a reducing agent sodium is but little inferior to potassium in energy, and since its combining number is lower, and the metal is much less expensive, it may generally be substituted for potassium with advantage in such operations.

Sodium has a bluish white colour; in appearance and properties it much resembles potassium, but is somewhat more volatile; it fuses at a temperature of 207°·7. It burns with a bright yellow flame. When dropped into cold water, it decomposes a portion of it, extricating hydrogen, but the gas does not take fire unless the water be heated previously.

The great storehouse of sodium is common salt, which is met with in nature in extensive deposits; it is also contained in vast quantities in the water of the ocean: the immense quantities of soda consumed in the arts are almost exclusively obtained from chloride of sodium, by a process presently to be described, though sodium occurs in several minerals, such as albite or soda-felspar, and cryolite, the double fluoride of sodium and aluminum. Borax or biborate of soda, and trona or the sesquicarbonate, as well as the nitrate, are also native compounds of soda.

(485) OXIDE OF SODIUM, or SODA ($NaO = 31$), forms the basis of the important series of salts of soda. It can be procured in an anhydrous state by burning the metal in dry air or oxygen gas; it is of a yellowish white colour, attracts moisture as greedily as the corresponding oxide of potassium, and this water cannot again be expelled from it by heat. In appearance and properties the hydrate closely resembles that of potash, and may be formed by a similar method; its affinity for acids, however, is less energetic. According to Filhol the solid hydrate (NaO,HO) has a *Sp. Gr.* of 2·13. The following table shows the proportion of anhydrous soda which is contained in solutions of soda of different densities:—

Strength of Solutions of Soda (Dalton).

Sp. gr.	NaO in 100 parts.	Sp. gr.	NaO in 100 parts.
1·56	41·2	1·32	23·0
1·50	36·8	1·29	19·0
1·47	34·0	1·23	16·0
1·44	31·0	1·18	13·0
1·40	29·0	1·12	9·0
1·36	26·0	1·06	4·7

Hydrate of soda is extensively used in the manufacture of hard soaps. A higher oxide regarded by Davy as a *sesquioxide of sodium* (Na_2O_3) may also be obtained.

The *sulphides* of sodium correspond in number with those of potassium, which they closely resemble. They may be prepared by analogous methods.

(486) Chloride of Sodium ($NaCl=58·5$); *Sp. Gr.* 2·011.—This important and well-known compound, formerly called *muriate of soda*, constitutes common culinary or table-salt. It is found native in the solid form, and it exists in solution in sea water in a proportion of about 2·7 per cent., which amounts to nearly 4 ounces per gallon, or to a bushel in from 300 to 350 gallons.

The extraction of the chloride from sea water was formerly practised to some extent upon the southern coast of our own island, but the manufacture is now unimportant, though in the southern countries of Europe the preparation of bay-salt is still a branch of industry of some magnitude. In conducting this process the sea water is allowed to run into shallow pools, in which the water evaporates and becomes concentrated by the heat of the sun: crusts of the salt are formed, and are raked off from time to time: the rough crystals thus obtained furnish the *bay-salt* of commerce. The concentrated sea water, or *bittern*, is employed as a source of bromine. Considerable quantities of magnesia are also extracted from it, as the chloride of magnesium, which is deliquescent, remains in solution. Balard, who has devoted much attention to the study of these mother-liquors, has devised a method of extracting from them not only sulphate of magnesia and chloride of magnesium, but also an important quantity of potash, in the form of a double sulphate of potash and magnesia, as well as of a double chloride of potassium and magnesium. (Regnault, *Cours de Chimie*, ii. 192, &c.) The process requires a careful attention to the temperature at which the crystallizations are effected. At temperatures below 27° the chloride of sodium still present in the brine decomposes the sulphate of magnesia, chloride of magnesium and sulphate of soda being formed; whilst at temperatures above 100° F., a sparingly soluble, double sulphate of soda and magnesia is formed.

Immense beds of common salt are met with in Cheshire, in Poland at Wielitzka, and at Cardona in Spain. It has also recently been found in abundance in the north of Ireland, near Belfast. Near Northwich, the principal deposit of rock salt in England, the mineral occurs in two beds, situated one above another, separated by about 30 feet of clay and marl intersected with small veins of salt: the two beds together are not less than 60 feet in

thickness, 300 yards broad, and a mile and a half long. These beds occur in magnesian limestone. The celebrated and beautiful mine of Wielitzka contains sufficient salt to supply the entire world for ages. It is calculated that the mass of rock salt here is 500 miles in length, 20 miles broad, and not less than 1200 feet in thickness. This salt deposit occurs in the chalk formation.* Chloride of sodium is sometimes found crystallized, and is then termed *sal gem*, or rock salt. The solubility of this chloride is frequently taken advantage of in diminishing the labour of raising the salt to the surface, water being let down into the bed of salt and allowed to remain till it has become saturated: it is then pumped out, and the brine is boiled down and crystallized. Some brine springs contain too small a portion of salt to render it profitable to effect the evaporation by heat; the water in these cases is therefore concentrated by *graduation*, as at Salzburg: this process consists in exposing the brine, diffused over a large surface, to the air, by pumping it up to a height, and then allowing it to trickle slowly over large stacks of fagots, piled in suitable buildings screened from rain, but freely exposed to the prevailing wind: after this process has been repeated eight or ten times, the solution acquires a density of about 1·140, and is sufficiently concentrated to allow the evaporation to be finished as usual by the direct application of heat. In the first basin an insoluble double sulphate of lime and soda is deposited, partly in the form of mud, or *schlot*, as the Germans term it, partly in the form of a hard scale, which adheres to the bottom of the pan: when the liquor reaches a density of 1·236 it is decanted into another pan, and evaporated; the crusts of salt are removed as they are formed.

The appearance of the salt varies according to the rate at which the evaporation is conducted; when the brine is boiled down rapidly, it furnishes the mealy, fine-grained salt used upon our tables; if evaporated more slowly, the hard, crystallized salt preferred for fishery purposes is obtained. The salt of commerce always contains a certain proportion of chloride of magnesium, which gives it a slightly deliquescent character, and adds to th pungency of its flavour. It is stated, that when the proportio of chloride of magnesium in the brine is considerable, the crysta of chloride of sodium form a scum over the surface which mu retards the evaporation. This inconvenience may be remedied the addition of a quantity of sulphate of soda, which decompo

* Some specimens of the salt from this mine decrepitate when thr into water, owing to the escape of condensed gas (C_2H_8, Rose), which is rated during the solution of the crystals.

the chloride of magnesium and converts it into sulphate of magnesia.

Properties.—Chloride of sodium has an agreeable, saline taste. It crystallizes in colourless transparent cubes, which are anhydrous, soluble in about 3 parts of cold water, and scarcely more soluble at a temperature of 212°; the saturated solution has a sp. gr. of 1·205. Water at 32° dissolves 35·5 per cent. of the salt, and 41·2 per cent. at 229°·5, the boiling point of the solution; 100 parts of the salt consist of 60·68 of chlorine and 39·32 of sodium. When heated suddenly, the crystals decrepitate with violence; at a bright red heat they fuse, and by a stronger heat are converted into vapour. Chloride of sodium is insoluble in pure alcohol, but is taken up in considerable quantity by dilute spirit. By exposing its aqueous solution to a temperature of about 14°, it crystallizes in hexagonal tables, which contain 4 or 6 Aq: as the temperature rises, the water is separated, the crystals fall to pieces, and become converted into a heap of minute cubes.

Chloride of sodium is consumed in large quantities in the manufacture of the salts of sodium, it is extensively employed in glazing stoneware, and is an article of daily domestic use, being indeed an essential constituent of the food both of man and of animals, who languish if it be supplied in insufficient quantity. The process of salting meat is resorted to on account of the powerfully antiseptic qualities of the chloride of sodium. In this operation a large quantity of the nutritive juice of the meat is extracted, and this liquid when saturated with the salt forms the *brine*. Meat thus prepared is much less digestible and nutritious than fresh meat.

(487) BROMIDE OF SODIUM ($NaBr = 103$) is analogous to bromide of potassium; it is soluble both in water and in alcohol, and crystallizes at temperatures above 86° in anhydrous cubes. At lower temperatures it forms hexagonal tables with 4 Aq.

IODIDE OF SODIUM ($NaI = 150$; *Sp. Gr.* 3·45) crystallizes in cubes, which are anhydrous: it occurs native in sea-water in minute proportion, but small as this proportion is, it furnishes the commercial supply of iodine: many marine plants appropriate it to their nutrition, and when these plants are burned, the iodide remains in the residue: the ash thus obtained goes by the name of kelp. A ton of good Irish kelp from drift weed furnishes about 8lb. of iodine.

(488) SULPHATE OF SODA ($NaO, SO_3 + 10\,Aq = 71 + 90$); *Sp. Gr. anhydrous,* 2·597, *crystallized,* 1·469.—This salt has long been known under the name of Glauber's salt. It crystallizes usually in long,

four-sided prisms, terminated by dihedral summits. It is remarkably efflorescent, and loses the whole of its 10 atoms of water by mere exposure, at common temperatures, to the atmosphere. It has a saline, bitter taste, and is occasionally used medicinally as a purgative. The crystallized sulphate contains 55·91 per cent. of water, 24·84 of acid, and 19·24 of soda; the anhydrous salt, 56·33 of acid, and 43·67 of soda.

The solubility of sulphate of soda in water offers some remarkable anomalies, which have been minutely investigated by Löwel.* It has already been mentioned (70) that a boiling, saturated

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* Three forms of sulphate of soda may be obtained in crystals, viz.—the anhydrous sulphate, the ordinary crystallized sulphate with 10 Aq., and another hydrate with 7 Aq., which crystallizes in rhombic prisms. Each of these varieties has a specific solubility. The 10-atom hydrate is the least soluble, and the 7-atom hydrate the most so of the three forms. The following table (Löwel, *Ann. de Chimie*, III. xlix. 50) exhibits the varying solubility of each form of the sulphate of soda, as the temperature rises :—

100 *Parts of Water when saturated contain, of*

Temp. F°.	Anhydrous salt.		Salt with 10 Aq.		Salt with 7 Aq.		
	Anhydr. =	with 10 Aq.	Anhydr. =	with 10 Aq.	Anhydr. =	with 7 Aq. =	with 10 Aq.
32			5·02	12·16	19·62	44·84	59·23
55·9			9·00	23·04	30·49	78·90	112·73
64·2	53·25	371·97	13·20	35·96	37·43	105·79	161·57
77·1	52·76	361·51	16·80	48·41	41·63	124·59	200·00
83·8	51·53	337·16	19·40	58·35	44·73	140·01	234·40
87·3	51·31	333·06	28·00	98·48	52·94	188·46	365·28
89·3	50·37	316·19	30·00	109·81	54·97	202·61	411·45
90·9	49·71	305·06	40·00	184·09			
93·0	49·53	302·07	50·76	323·13			
104·3	48·78	290·00	55·00	412·22			
113·1	47·81	275·34					
122·7	46·82	261·36					
139·6	45·42	242·89					
159·3	44·35	229·87					
184·0	42·96	213·98					
217·7	42·65	210·67					

From this table it appears that the solubility of the anhydrous salt decreases from 64°·4 to the boiling point (217°·7) of the solution. Below 64° the molecular constitution of the salt is changed, a saturated solution depositing, in vessels from which air is excluded, crystals of the 7-atom hydrate. 100 parts water at 64°·4 retain as much as 53·25 of the anhydrous salt, whilst at the boiling point only 42·65 parts are held in solution. Hence if a solution saturated at 64° be simply heated to boiling, without allowing any loss of liquid by evaporation, it will deposit in hard, gritty, anhydrous crystals more than one fifth of the salt which it previously held in solution.

In the case of the least soluble form of the sulphate, the 10-atom hydrate, the solubility increases until the temperature reaches 93°, at which point the salt begins to liquefy in its water of crystallization: its molecular constitution

solution of this salt, if closed hermetically, may be kept for months without crystallizing, but the moment that air is admitted, the whole becomes semi-solid, from the sudden formation of crystals through the mass. It is most probable that the salt exists in the supersaturated solution in the form of the anhydrous salt, and that crystallization occurs when any circumstance occasions the formation of the less soluble 10-atom hydrate. The crystallization of such a solution may, for example, be instantly determined by dropping in a fragment of the sulphate or by contact with a rod of glass or of metal. If, however, the glass rod or the metallic wire be boiled with water, and allowed to cool under water or in a closed vessel, it may be introduced into the supersaturated solution without causing the crystallization of the salt.

Sulphate of soda is soluble in hydrochloric acid, with great depression of temperature. A convenient freezing mixture is obtained by pouring 5 parts of the commercial acid upon 8 of the crystallized sulphate.

Sulphate of soda, to which the name of *Thénardite* has been

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then undergoes a change, and it becomes gradually converted into the anhydrous variety, which at that particular temperature has a lower solubility than the hydrated salt, and consequently is partially separated in crystalline grains.

The hydrate with 7 Aq is more soluble than either of the foregoing forms; but under ordinary circumstances it cannot exist in contact with the atmosphere, and is only deposited from supersaturated solutions in closed vessels, or in flasks which have been allowed to cool covered with small capsules, so as to prevent the entrance of particles of dust or of foreign matter. Crystals of the 7-atom hydrate may also be obtained by pouring a boiling solution of the sulphate into a capsule, and allowing it to cool under a bell glass, over a vessel of chloride of calcium. In whatever mode the crystals of the 7-atom hydrate have been produced, they undergo change from very slight causes, and become white and opaque with evolution of heat, either when exposed to the air or when the solution is allowed to crystallize around them, or when touched with a glass rod. The solubility of the 7-atom hydrate rises with the temperature, as is shown in the table; but this form of the salt cannot exist at temperatures above 84°: for when heated to this point its crystals begin to liquefy in their water of crystallization; and, in consequence of a molecular change, crystals of the anhydrous variety are deposited.

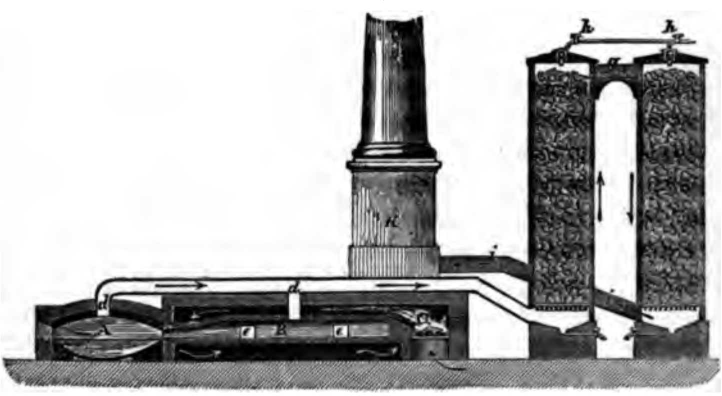
From the foregoing details it will be easy to perceive why it is that a hot solution of the sulphate deposits crystals so slowly. When a solution of sulphate of soda, saturated at its boiling point, is poured into an open capsule, a film of crystals of the anhydrous sulphate is formed at first upon its surface, owing to the rapid evaporation of a portion of the solvent. No crystals, however, are deposited in the body of the liquid until the temperature has fallen to about 91°. The film of crystals first formed is gradually redissolved, and crystals of the 10-atom hydrate are formed as the temperature continues to fall. If the solution be evaporated at temperatures above 93°, acute rhombic octohedra of the anhydrous salt are produced: but if a boiling saturated solution be allowed to cool in closed vessels, no crystals are deposited until the temperature falls to 64°, when oblique rhombic prisms of the 7-atom hydrate are formed.

given, has been met with nearly pure not far from Madrid, deposited at the bottom of some saline lakes, in anhydrous octohedra. It has likewise been found, not far from the same place, combined with sulphate of lime, as *Glauberite*, in anhydrous crystals.

Crystallized sulphate of soda also frequently occurs in needles as an efflorescence upon plaster, and upon brickwork in damp situations.

Preparation.—Sulphate of soda is made from oil of vitriol and common salt in enormous quantities, under the name of *salt-cake*, as a preliminary step in the manufacture of carbonate of soda. The operation is carried on in a reverberatory furnace, connected with an apparatus for condensing the hydrochloric acid, which, till within the last few years, was allowed to escape into the atmosphere, to the serious injury of vegetation in the surrounding district. One of the best forms of furnace is shown in section in fig. 314: the course of the flues, however, is not exactly such as

FIG. 314.



is there represented: A, the smaller of the two compartments which compose the furnace, is of cast iron; into this (the *decomposer*) from 5 to 6 cwt. of common salt are introduced, and an equal weight of sulphuric acid, of specific gravity 1·6, is gradually mixed with it; a gentle heat being applied to the outside, enormous volumes of hydrochloric acid gas are disengaged, and pass off by the flue, *d*, to the condensing towers, E and F; these towers are filled with fragments of broken coke or stone, over which a continuous stream of water is caused to trickle slowly from *h*, *h*. A steady current of air is drawn through the furnace and condensing towers, by connecting the first tower with the second, as represented at *g*, and the second tower with the main chimney, K, of the works. In the first bed of the furnace, about half the

hydrochloric acid is expelled from the salt: the pasty mass thus produced is then pushed through a door for the purpose into the *roaster*, or second division, B, of the furnace. In this state it consists of a mixture of bisulphate of soda and undecomposed salt. The reaction in the first bed of the furnace may be represented as follows:—

$$2\ NaCl + 2\ (HO,SO_3) = NaCl + HO,NaO,\ 2\ SO_3 + HCl.$$

In the second stage of the operation a higher temperature is required; the bisulphate of soda then reacts upon the unchanged chloride, and the conversion into neutral sulphate of soda is complete; thus $NaCl + HO,NaO,\ 2\ SO_3 = HCl + 2\ (NaO,SO_3)$. The hydrochloric acid gas, as it is liberated from B, passes off through the flue, *d*, and is carried on to the condensing towers. Heat is applied to the outside of the roaster, B; the smoke and products of combustion circulate in separate flues around the chamber, in the direction indicated by the arrows, but never come into contact with the salt-cake in B.

Sulphate of Potash and Soda [$NaO,SO_3 + 3\ (KO,SO_3)$, Penny; *Sp. Gr* 2·668].—This double salt is anhydrous; it may be formed by dissolving the two salts in water and evaporating. Gladstone has shown that the employment of a large excess of sulphate of soda does not alter the composition of the salt, the sulphate of soda in excess crystallizing in its usual form.

It is obtained upon a large scale from kelp liquors during the manufacture of iodine, and is known under the name of *plate sulphate*, from the manner in which it is deposited in hard crystalline layers or plates, upon the sides of the crystallizing vats. During the act of crystallizing it emits vivid scintillations of phosphorescent light: this phosphorescence is most striking when the temperature is near 100° F. A very brilliant effect is produced by dashing a pailful of the warm mother-liquor upon a crop of crystals in a vat from which the mother-liquor has been drained off a few hours previously.

A *Bisulphate of Soda* ($NaO,HO,\ 2\ SO_3 = 120$; *Sp. Gr.* 2·742) corresponding to bisulphate of potash, may be formed. It is more easily deprived of basic water by heat than the bisulphate of potash. The anhydrous salt, by a stronger heat loses its second equivalent of sulphuric acid, and may be employed as a convenient source of anhydrous sulphuric acid.

(489) SULPHITE OF SODA ($NaO,SO_2 + 7\ Aq. = 63 + 63$; *Sp. Gr.* 1·736) is now prepared largely under the name of *antichlore*, for the purpose of removing the last traces of chlorine from the

bleached pulp obtained from rags in the manufacture of paper. It is procured by passing sulphurous acid, obtained by the combustion of sulphur in air, over moistened crystals of carbonate of soda, so long as the acid gas is absorbed; the mass is dissolved in water and crystallized. Sulphite of soda forms efflorescent, oblique prisms, which fuse at 113°; they are soluble in about 4 parts of cold water: the solution has a slightly alkaline reaction and a sulphurous taste.

A *Bisulphite of Soda* ($NaO,HO, 2\,SO_2$) may be obtained in crystals.

(490) NITRATE OF SODA, or *Cubic Nitre* ($NaO,NO_5=85$; *Sp. Gr.* 2·182), occurs abundantly on the surface of the soil, in the district of Atacama, in Peru, as nitre does in the East Indies. It is a somewhat deliquescent salt, and is soluble in about twice its weight of cold water; it crystallizes in obtuse rhombohedra, and has a cooling, saline taste. When heated, it fuses at 591°, and at a higher temperature it undergoes decomposition. It is employed in the manufacture of nitric and sulphuric acids, but from its deliquescence cannot be substituted for nitrate of potash in gunpowder. It is frequently used as a manure, as in top-dressing barley.

(491) CARBONATE OF SODA ($NaO,CO_2+10\,Aq=53+90$); *Sp. Gr., anhydrous,* 2·427, *hydrated,* 1·454.—The preparation of this salt constitutes one of the most important branches of chemical manufacture in this country, immense quantities of it being consumed in the production of glass, in the fabrication of soap, and in the preparation of the various compounds of sodium, besides a considerable consumption as a detergent by the calico printer, as well as in the laundry for softening hard waters by precipitating the salts of lime and magnesia.

The greater portion of the carbonate of soda formerly employed was obtained from *barilla*, which is the ash furnished by burning marine plants. The *Salsola soda* was extensively cultivated for this purpose on the southern coast of Spain, and on being burnt, it yields a semi-vitrified mass, which contains from 25 to 30 per cent. of carbonate of soda. The *Salicornia* was cultivated for a similar purpose on the southern coast of France; but these sources of supply have almost entirely given way to a process by which the carbonate may be manufactured from sea-salt.

Manufacture.—In the process of manufacture a rough sulphat of soda is first formed, in the manner already described (488). Tl sulphate of soda is then mingled with chalk and powdered coal the proportion of about 3 parts of sulphate of soda, 3 of chalk, a

$1\frac{1}{2}$ or 2 of coal; this mixture is thrown, in quantities of about $2\frac{1}{2}$ cwt. at a time, into a hot reverberatory furnace, and frequently stirred, until the mass is thoroughly melted.

As the furnace, fig. 315, is constructed with two doors, D, E,

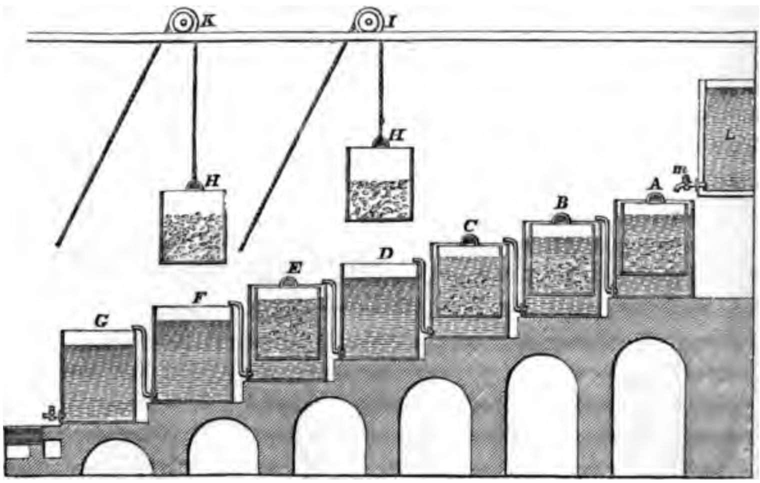
FIG. 315.

and a double floor, B, C; one charge is introduced at the further door, E, whilst another, nearer the fire, is fusing at B: towards the conclusion of the operation the mass melts, and effervesces violently from the escape of carbonic oxide gas, which burns with a greenish or yellow flame; the mass is stirred briskly for a few minutes, and when completely and tranquilly fused, is raked out into a square trough or mould; when cold, this loaf is turned out and forms *ball soda*, or *black ash*, containing from 20 to 27 per cent. of pure soda, mixed with oxysulphide of calcium and unburned coal. In order to extract the salts of soda from it, the black ash is broken up into coarse fragments, and digested with warm water for six hours, in vats provided with false bottoms: this washing is systematically carried on till the soluble portions are extracted, the last washings being employed to act upon fresh portions of ball soda.

One of the best forms of apparatus for the lixiviation of ball soda is shown in fig. 316. The principle on which it is constructed is simple, but it admits of extensive application; for in many cases much of the economy of a manufacturing process depends upon the systematic washing of the product in such a manner as to extract the largest amount of soluble matter by means of the smallest quantity of water. In the case before us this is effected by placing the material for lixiviation,—the black ash, in perforated sheet-iron vessels, H, H, which can be raised or lowered into outer

lixiviating vessels, also made of iron, by means of the cords and pulleys, I, K. When a charge is received from the furnace it is

FIG. 316.



introduced into the lowest vessel, G, where it is submitted to the dissolving action of a liquid already highly charged with alkali by digestion upon the black ash contained in the tanks above it: after a certain time this charge is raised by the rope from G into the tank F, where it is submitted to a weaker liquid, and so on, successively. The alkali at each stage becomes more completely exhausted, and the residue is successively submitted to the action of weaker ley, till at length, in A, it is acted upon by water only, supplied from the cistern L. When fresh water is admitted from *m*, to the top of the vessel, A, as it is specifically lighter than the saline solution, it lies upon its surface, and gradually displaces the solution from A, through the bent tube, whilst the water takes its place; the liquid from A acts in a similar manner upon that contained in B; and this displacement proceeds simultaneously through each successive tier of the arrangement, until the concentrated ley flows off from G, and is transferred to the evaporating pans.

Almost the whole of the sulphur originally present in the salt-cake is retained in the insoluble residue in the form of sulphide of calcium, together with the excess of lime and coal employed. It accumulates at the soda works till it forms a mountain of *soda waste*, to the annoyance both of the neighbourhood and of the manufacturer.

The water for lixiviation must not be employed at a temperature exceeding 110°; if it be, it decomposes the oxysulphide of

calcium. The black solution thus obtained is allowed to settle, and is then pumped up into large shallow iron pans, where it is evaporated by the waste heat from the black-ash furnaces. A large portion of the salt crystallizes during the ebullition, and is removed by means of perforated ladles. In order to convert the caustic soda which the solution contains into carbonate, it is evaporated to dryness, and, after being mixed with about $\frac{1}{7}$th of its weight of sawdust, is roasted in a reverberatory furnace: most of the sulphur escapes during this operation in the form of sulphurous acid; the residue yields the *soda ash*, or alkali of commerce, which contains about 52 per cent. of pure caustic alkali. If required in crystals, the crude carbonate thus obtained is redissolved, the liquid allowed to settle, and, while hot, is run into deep pans, capable of containing 150 gallons of liquid, and about a ton of crystallized carbonate. The liquid cools in the course of five or six days, and crystals of large size are formed; the mother-liquor, which is drained off by withdrawing a plug in the bottom, is then further evaporated down, and yields an ash of inferior quality.

The preparation of carbonate of soda, therefore, comprises three principal operations:—

1st. The production of *salt-cake*, or crude sulphate of soda, from common salt, by the action of sulphuric acid.

2nd. The making of *black ash*, or impure carbonate of soda, mixed with sulphide of calcium, by deoxidation of the salt-cake after mixture with chalk, by means of carbon.

3rd. The preparation of *soda ash*, or the separation of the carbonate of soda from the black ash by lixiviating the latter in warm water and evaporating the solution to dryness.

Of these operations the most remarkable is the preparation of the black ash, by fusion of the sulphate with chalk and coal. The chemical changes which occur consist, first, in the deoxidation of the salt-cake, and its conversion into sulphide of sodium with evolution of carbonic oxide; and, secondly, in the formation of carbonate of soda and sulphide of calcium by interchange of the constituents of the sulphide of sodium and the carbonate of lime; the sulphide of calcium being rendered completely insoluble by the excess of lime employed. These reactions occur simultaneously, and may be represented in the following equation (omitting the excess of lime):—

$$NaO,SO_3 + 4\,C + CaO,CO_2 = NaO,CO_2 + CaS + 4\,CO.$$

An excess both of coal and of chalk is always employed in practice, as a good deal of coal burns off unavoidably, and an excess

of lime is needed, to render the sulphide of calcium insoluble. Many attempts have been made to recover the sulphur from the soda waste, but hitherto without commercial success.

Various processes have, from time to time, been proposed, to supersede the one just described, which was invented by Leblanc; and of late years works on a considerable scale have been established, in which, by roasting iron or copper pyrites directly with chloride of sodium, a sulphate of soda has been obtained without the preliminary manufacture of oil of vitriol, whilst chlorine is evolved. The reaction with iron pyrites is, $2\ FeS_2 + 4\ NaCl + 19\ O = Fe_2O_3 + 4\ (NaO, SO_3) + 4\ Cl$. A portion of the sulphur, however, always burns off in the form of sulphurous acid. By the employment of poor ores of copper and tin, it has been found possible to extract these metals with advantage from materials which would not otherwise have paid for working.

Tilghman takes advantage of the decomposition of chloride of sodium in the presence of alumina, by steam at a high temperature, in order to obtain alkali from it. Precipitated alumina is made up into balls with chloride of sodium, and exposed to a current of steam in a reverberatory furnace strongly heated. Hydrochloric acid is expelled, whilst soda is formed, and combines with the alumina: $NaCl + Al_2O_3 + HO = NaO,Al_2O_3 + HCl$; when cold, the compound of alumina and soda is decomposed by a current of carbonic acid, and the carbonate of soda is dissolved from the alumina, which may be again employed for the same purpose.

Properties.—Carbonate of soda has a nauseous alkaline taste; it is an efflorescent salt, usually crystallizing in large, transparent, rhomboidal prisms, which contain 62·93 per cent. of water, 21·68 of soda, and 15·39 of carbonic acid; they are soluble in any proportion in hot water, and even melt in their water of crystallization; they are also very soluble in cold water. The salt readily parts with its water, and melts at a red heat: it then contains 58·49 per cent. of soda and 41·51 of carbonic acid. If crystallized at a temperature of $-4°$, an unstable hydrate with 15 Aq may be obtained (Jacquelain). Mitscherlich has also obtained carbonate of soda crystallized with 6 Aq. If crystallized above 93°, the salt is deposited in forms derived from the square-based octohedron, which contain 5 Aq; whilst, if crystallized between 158° and 176°, four-sided prisms are produced, which contain only 1 Aq (Berzelius). Solutions of carbonate of soda may, according to Löwel (*Ann. de Chimie*, III. xxxiii. 382), be obtained in the condition of supersaturation, by adopting precautions similar to those mentioned when speaking of the sulphate.

The carbonate exhibits a maximum solubility at 100° F.; the decrease of solubility above this point arises from the formation of another hydrate (NaO,CO_2+Aq) which is deposited when a solution saturated at 219° is concentrated by boiling.*

(492) *Bicarbonate of Soda* ($NaO,HO, 2\,CO_2=84$; *Sp. Gr.* 2·192) is obtained by saturating a strong solution of the neutral carbonate with carbonic acid; the solid crystallized carbonate also absorbs carbonic acid with considerable evolution of heat, and as the bicarbonate is less soluble than the carbonate, this process is employed for procuring pure carbonate from the commercial crystals; for on washing the powdered bicarbonate with cold water till the washings are free from sulphates and chlorides, a pure bicarbonate is obtained. This salt is thus manufactured upon a large scale, by exposing crystallized carbonate of soda in stone or wooden boxes to a current of carbonic acid gas: the water of crystallization is separated during the process, and the temperature rises considerably. The bicarbonate crystallizes in rectangular four-sided prisms, which require 10 parts of water for solution at ordinary temperatures. If its solution be heated, it loses one half of the additional equivalent of carbonic acid, and is converted into sesquicarbonate. At a red heat the salt is converted into the normal carbonate (NaO,CO_2).

* This hydrate is more soluble in cold than in hot water, and becomes redissolved in the mother-liquor if allowed to cool. The supersaturated solution contains a hydrate with 7 Aq. Löwel describes two modifications of this 7-atom hydrate, which differ in solubility and in crystalline form: one variety, *a*, is deposited in rhombohedral crystals, if a solution saturated at the boiling point be corked whilst boiling, and allowed to cool down to between 50° and 60°, but it is redissolved on raising the temperature to 70°; and on cooling down to between 40° and 50°, the modification *b* is deposited in square tables. If cooled below 40° the solution gradually deposits the 10-atom hydrate, and the condition of supersaturation ceases. The following table gives a comparative view of the quantities of the 10-atom hydrate, and the two varieties of the 7-atom hydrate contained in 100 parts of the saturated solutions at different temperatures:—

100 *parts of Water, when saturated, contain, of*

Temp. °F.	NaO,CO_2+10 Aq.		NaO,CO_2+7 Aq (*b*).			NaO,CO_2+7 Aq (*a*).		
	Anhydr. salt.	Crystd. salt.	Anhydr. salt.	Crystd. with 7 Aq. *b*.	Crystd. with 10 Aq.	Anhydr. salt.	Crystd. with 7 Aq. *a*.	Crystd. with 10 Aq.
32	6·97	21·33	20·39	58·93	84·28	31·93	112·94	188·37
50	12·06	40·94	26·33	83·94	128·57	37·85	150·77	286·13
59	16·20	63·20	29·58	100·00	160·51	41·55	179·90	381·29
68	21·71	92·82	38·55	122·25	210·58	45·79	220·20	556·71
77	28·50	149·13	38·07	152·36	290·91			
86	37·24	273·64	43·45	196·93	447·93			
100·4	51·67	1142·17						
219·2	45·47	539·63						

A native *Sesquicarbonate of Soda* ($2\,NaO,HO, 3\,CO_2+3\,Aq = 137+27$), which, however, always contains sulphate of soda and chloride of sodium, has been long known in commerce as *trona* or *natron:* it is chiefly obtained as a saline efflorescence on the borders of some lakes, of which those of Egypt are the best known. Many other countries, however, such as those in the neighbourhood of the Black and the Caspian Seas, as well as some parts of Thibet and of Siberia, also furnish this salt. It crystallizes in rhombic prisms, terminated by four-sided pyramids; it is less soluble than the carbonate, but more so than the bicarbonate, and has a feebly alkaline reaction.

The carbonates of soda and potash, when melted together in the proportion of 1 equivalent of each, readily combine and form a salt which fuses at a lower temperature than either of its components. On account of its ready fusibility, this mixture is preferred to carbonate of potash or carbonate of soda alone, as a means of decomposing siliceous minerals in analytical operations (479). If carbonate of soda be dissolved in a solution of carbonate of potash in excess, the solution, on evaporation, yields transparent crystals which, according to Margueritte, consist of $2\,(NaO,CO_2)+KO,CO_2+18\,Aq$: this salt is decomposed if it be attempted to recrystallize its aqueous solution, carbonate of soda being deposited.

(493) PHOSPHATES OF SODA.—Phosphoric acid forms with soda several crystallizable salts: some account has already been given of these compounds (370, 371, 372).

Neutral Tribasic Phosphate, or Subphosphate of Soda ($3\,NaO, PO_5+24\,Aq=164+216$); *Sp. Gr. cryst.* 1·622.—This salt is prepared from the rhombic phosphate by adding caustic soda to its solution till it feels soapy to the fingers. It crystallizes readily in small prisms, which effloresce in the air, and gradually absorb carbonic acid. A remarkable double salt of this phosphate with fluoride of sodium ($NaF, 3\,NaO,PO_5+24\,Aq$) was obtained by Briegleb, by fusing the rhombic phosphate of soda with fluoride of calcium and carbonate of soda; and also by digesting powdered cryolite with a mixture of phosphate of soda and caustic soda.

Rhombic Phosphate of Soda ($2\,NaO,HO,PO_5+24\,Aq=142+216$); *Sp. Gr. cryst.* 1·586; Kopp.—This salt is the one from which most of the phosphates are formed: it is the one which has been longest known, and is that commonly called phosphate of soda. It is best procured by neutralizing with carbonate of soda the acid phosphate of lime, prepared as directed for obtaining phosphorus (365); by this means carbonate of lime is precipitated, and allowed to subside; the clear liquid is then decanted

from the precipitate, and set aside to crystallize. Phosphate of soda forms large, transparent, efflorescent rhombic prisms: they have a cooling saline taste, and are soluble in 4 parts of cold water; at 99° they fuse in their water of crystallization, and are therefore soluble in boiling water to an unlimited extent; the solution has a faintly alkaline reaction. It corrodes flint-glass bottles, and occasions the separation of white siliceous flakes from their surface. Clark found that when the solution of this salt is evaporated at temperatures above 90°, the salt crystallizes with 14 atoms of water, and is not efflorescent; in both forms it is isomorphous with the corresponding arseniate of soda. If heated to 300°, it loses all its water of crystallization; but if redissolved in water, it may be obtained from its solution with all its characteristic properties. If a solution of this phosphate be mixed with free phosphoric acid, until it ceases to precipitate chloride of barium, another phosphate is produced, formerly known as the *biphosphate of soda* ($2\,HO,NaO,PO_5+2\,Aq=120+18$); it crystallizes with difficulty in right rhombic prisms, and has a strongly acid reaction.

All these are tribasic phosphates; they precipitate nitrate of silver of a yellow colour.

Pyrophosphate of Soda ($2\,NaO,PO_5+10\,Aq=133+90$); *Sp. Gr. cryst.* 1·836.—If the rhombic phosphate be ignited, it loses all its water, and on then treating it with water, a new dibasic salt is dissolved, which crystallizes in prisms. Its solution has an alkaline reaction, and yields a dense white precipitate with nitrate of silver, which is not changed by exposure to light.

Metaphosphate of Soda ($NaO,PO_5=102$).—If microcosmic salt, or if the acid tribasic phosphate, or the acid pyrophosphate of soda be heated to redness, all the volatile bases are expelled, the residue fuses to a clear glass, and on redissolving, the metaphosphate or monobasic phosphate of soda is obtained. It forms a deliquescent and very soluble salt, which has a feebly acid reaction upon litmus. It cannot be obtained in crystals. The solution of this salt causes, with nitrate of silver, a white gelatinous precipitate, soluble in excess of the metaphosphate; with nitrate of baryta or of lime a similar gelatinous precipitate is formed. This salt is susceptible of various modifications by the application of different temperatures (372).

(494) BIBORATE OF SODA ($NaO,\,2\,BO_3+10\,Aq=101+90$; *Sp. Gr. fused,* 2·367, *cryst.* 1·740), is well known in commerce under the name of *borax*. It is produced in considerable quantities in various parts of the world, particularly in Thibet, whence

for many years the principal part of the borax consumed was supplied. The crude borax, or *tincal,* is obtained by the spontaneous evaporation of the waters of the lakes whence it is derived, and occurs crystallized in flattened six-sided prisms, terminated by trihedral summits. These crystals are, however, very impure, being covered with a greasy coating, said to be derived from the skins in which they are imported. In order to remove this grease, the crystals are powdered, thrown upon a filter, and washed with a weak solution of caustic soda, which forms a soap with the grease, and dissolves it; the remaining salt is dissolved in water. Carbonate of soda equal to one eighth of the weight of the borax is added to the solution; a copious precipitate of earthy impurities ensues, the liquid is cleared by filtration, and allowed to cool very slowly: the borax is deposited in rectangular or in six-sided prisms, containing 10 Aq: 100 parts of this salt contain 36·65 of boracic acid, 16·23 of soda, and 47·12 of water. When rendered anhydrous by heat, it contains 69·3 per cent. of boracic acid, and 30·7 of soda.

A large quantity of borax is now manufactured from the boracic acid obtained from the lagoons of Tuscany, by saturating it with carbonate of soda, and allowing the salt to crystallize. In the course of this operation the crude boracic acid is mixed with about half its weight of soda ash, and is thrown in quantities of about 3 cwt. at a time upon the floor of a reverberatory furnace; the mixture soon frits and effervesces, and must be well stirred during the process: a quantity of carbonic acid, of ammonia, and of organic matter which always accompanies the boracic acid, is got rid of in this operation. The fritted mass is then lixiviated in deep iron boilers. Here the solution is allowed to remain at rest, in order to allow the impurities—which consist chiefly of alumina, carbonate of lime, and some silica—to subside: and the liquid, when brought to the sp. gr. 1·166, is drawn off into wooden tanks, lined with lead, where the solution cools very slowly. The large crystals in which borax is demanded for the market can be procured only by operating on very large masses of the salt. Borax may also be obtained in octohedral crystals with 5 Aq, if the salt be allowed to crystallize from a solution of sp. gr. 1·256, at a temperature between 174° and 133°.

Borax has a feebly alkaline taste and reaction. The prismatic crystals are soluble in about half their weight of boiling water, and in 12 parts of cold water: they are slightly efflorescent. When heated, borax bubbles up, loses its water, and melts below redness into a transparent glass; this glass dissolves many metallic oxides

which often impart intense and characteristic colours to the bead. Borax is hence much used as a test before the blowpipe for recognising the presence of certain metallic oxides. For this purpose a small crystal of borax is fused upon the end of a bent platinum wire, and a minute quantity of the substance to be tested is melted with the salt in the flame of the blowpipe: the colour of the glass varies according as the bead is heated in the oxidizing or in the reducing flame (404). The power which this salt possesses of dissolving the metallic oxides renders it advantageous, in the process of soldering oxidizable metals, to sprinkle the metallic surfaces with powdered borax; on the application of heat the borax melts as well as the solder, and the film of oxide which would otherwise prevent the adhesion, is removed from the pieces of metal at the moment that the alloy is presented to unite them. Borax is used in the arts as a flux, and by the refiner in the melting of gold and silver. In making enamels it is frequently added for the purpose of rendering the compound more fusible, and it is largely employed in fixing colours on porcelain.

Other borates of soda may be formed, but the biborate is the only salt of any practical importance; the quadriborate ($NaO, 4\,BO_3$) crystallizes with great difficulty: a neutral borate may be obtained by fusing 1 atom of ordinary borax with 1 of carbonate of soda; it crystallizes in oblique prisms ($NaO, BO_3 + 8\,Aq$).

(495) Silicates of Soda.—When finely divided silica is gradually added to fused carbonate of soda, carbonic acid is evolved with effervescence, and a mixture of various silicates of soda is formed. Fritsche obtained a neutral silicate ($NaO, SiO + 9\,Aq$), by dissolving in a strong solution of hydrate of soda a quantity of silica equal in weight to the anhydrous soda present in the liquid: it crystallizes sometimes with 6, sometimes with 9, atoms of water. When a concentrated solution of carbonate of soda is boiled with finely divided silica, a large proportion of silica is dissolved; but the clear liquid as it cools deposits a gelatinous precipitate, which, according to Forchhammer, consists of $NaO, 36\,SiO_2$. Other silicates have been obtained, to which the formulæ ($2\,NaO, 5\,SiO_2$), ($NaO, 3\,SiO_2$) and ($NaO, 4\,SiO_2$) have been assigned. It is difficult, however, to prove the existence of the three compounds last named. The neutral silicate has the property of being dissolved by an excess of fused carbonate of soda, and the glass, which is clear and transparent while hot, becomes opaque on cooling; but the same silicate, if heated sufficiently with an excess of silicic acid, melts, and forms a homogeneous mixture, which yields a transparent glass on cooling, the fusibility decreasing as the pro-

portion of silica increases, until when the quantity of silica amounts to 9 equivalents, the heat of a forge is required for its fusion. These silicates are all more or less soluble in boiling water.

A peculiar silicate, which has received the name of *soluble glass*, is prepared by melting together 8 parts of carbonate of soda, or 10 of carbonate of potash, with 15 of pure quartz sand and 1 part of charcoal (Fuchs); the charcoal reduces the carbonic acid to carbonic oxide, and facilitates the decomposition of the alkaline carbonate: a black glass is thus obtained, which is not soluble in cold water, but is almost completely dissolved by 5 or 6 times its weight of boiling water. Soluble glass is employed in fixing fresco colours, by the process known as *stereochromy*. The ground employed in this process for the reception of the colour consists of a mixture of lime and fine sand, cemented by a solution of soluble glass. The colours, ground up with water, are then applied and a varnish of soluble glass is brushed over the whole.

Allusion has already been made to the application of a solution of soluble glass as a cement in the preparation of an artificial siliceous stone (385). Many metallic oxides—such as lime, magnesia, and oxide of zinc—are acted upon by the solution of silicate of soda, carbonate of lime and other salts being converted by it into masses of great hardness and durability; double decomposition of the silicate and earthy salt occurring to a greater or less extent. Upon this principle, Mr. Ransome has applied a solution of silicate of potash to the prevention of the decay of magnesian and other limestones which are exposed to the weather: a solution of the silicate is brushed over the surface of the stonework, which becomes gradually converted superficially into silicate of lime.

When heat is applied to the silicates of the alkalies, they do not at once become liquid, but pass through an intermediate viscous stage: they impart this viscidity, and the transparency which they preserve on cooling, to many other silicates if they are fused with them, and they destroy the tendency to crystallize on solidifying which the silicates of the earths and of the heavy metallic oxides possess. This property is of the highest importance to mankind, for upon it depends the most valuable properties of glass—ductility, which enables it to be moulded whilst in this intermediate state, and transparency, which renders it applicable to a multitude of important uses. The silicates of the alkalies are unable alone to resist the action of water and other solvents sufficiently to fit them for many of the applications of glass; but when combined with silicates of the earths and certain metallic oxides,

mixtures may be obtained after fusion which are no longer soluble in water or in acids.

Glass.

(496) The composition of glass differs considerably with the nature of the purposes to which it is destined, but it consists mainly of mixtures, in varying proportions, of silicates of potash, soda, lime, baryta, magnesia, alumina, and oxide of lead, coloured by the addition of small quantities of different metallic oxides, particularly those of iron, manganese, cobalt, uranium, and gold.

The degree of fusibility of these different silicates varies considerably. The silicates of lime and of magnesia fuse with great difficulty when heated *per se:* the most fusible compound contains 2 atoms of base to 3 of acid, the quantity of oxygen in the base, being to that in the silicic acid as 1 is to 3. The silicates of protoxide of iron, $2\ FeO, 3\ SiO_2$, and of manganese, are readily fused, and crystallize on cooling. The silicate of lead, $2\ PbO, 3\ SiO_2$, is still more fusible, and on cooling forms a yellow transparent glass. On the other hand, silicate of alumina, $Al_2O_3, 2\ SiO_2$, is nearly infusible in the furnace. All these silicates, however, when mixed with each other, or with the silicates of the alkalies, melt at considerably lower temperatures, the fusing point being generally much below that of the mean of the different silicates employed. The silicates of lime and alumina are nearly infusible when separate, but they melt readily after they have been mixed together.

Many of the properties of glass are familiar to every one. It is a transparent brittle solid, more or less fusible, and just before fusion possessed of remarkable ductility, a property which enables the workman to fashion it into the numberless forms which luxury or convenience dictates. The different varieties of glass are not to be regarded as definite compounds, but as mixtures of various silicates in different proportions, with an excess of silica. It is generally found, however, in the best kinds of glass, that the mixtures are very nearly in such proportions that but little silica remains in the uncombined form. The proportion of silica to the bases is most conveniently expressed by ascertaining the proportion which the oxygen of the bases bears to that of the silicic acid. The subjoined table gives the result of some analyses of the more important kinds of glass:—

Composition of different Varieties of Glass in 100 parts.

	Dumas.		Richardson.	Dumas.	Berthier.	Rowney.
	Bottle.	Window.		Plate.		Glass tube.
	French.	French.	English.	French.	Venetian.	Bohemian.
Silica	53·55	69·65	66·37	73·85	68·6	73·13
Potash	5·48	...	...	5·50	6·9	11·49
Soda	...	15·22	14·23	12·05	8·1	3·07
Lime	29·22	13·31	11·86	5·60	11·0	10·43
Magnesia	...	...	...	...	2·1	0·26
Alumina	6·01	1·82	8·16	3·50	1·2	0·30
Oxide of iron	5·74	...	...	...	0·2	0·13
Oxide of manganese	...	...	...	...	0·1	0·46
Ratio of the oxygen in the bases to that in the silica	1 : 2	1 : 4	2 : 7	1 : 7	1 : 5	1 : 6

	Dumas.		Faraday.	Dumas.		
	Bohemian goblet.	Crown.	English flint.	Guinand's optical.	Strass.	Enamel.
Silica	69·4	62·8	51·93	42·5	38·1	31·6
Potash	11·8	22·1	13·77	11·7	7·9	8·3
Lime	9·2	12·5	...	0·5		
Alumina	9·6	2·6	0·47	1·8	1·0	
Oxide of lead	...	...	33·28	43·5	53·0	50·3
Oxide of tin	...	...	...	...	...	9·8
Oxides of iron and manganese	...	...	0·27			
Ratio of the oxygen in the bases to that in the silica	1 : 4	1 : 5	1 : 6	1 : 4	2 : 7	3 : 7

(497) *Glass in which Silicates of Potash and Lime predominate.*—The silicates of potash and lime are the principal components of the celebrated Bohemian glass, including the variety which is employed in the preparation of the hard glass of difficult fusibility, so much prized in the laboratory in the tubes used for the combustion of organic compounds: the composition of this glass may be represented approximatively by the formula ($KO, 3\ SiO_2 + CaO, 3\ SiO_2$), part of the potash having its place supplied by soda, and part of the lime by magnesia, alumina, and traces of the oxides of iron and manganese. The more fusible glass which is employed in the manufacture of the beautiful ornamental objects for which Bohemia has long been distinguished, contains silicate of alumina,

with silicates of potash and lime, in a proportion which approaches [$KO,SiO_2 + 2(CaO,SiO_2) + Al_2O_3, 3\ SiO_2$]. The crown glass, employed for optical purposes, has nearly the formula ($KO,SiO_2 + CaO,SiO_2$). (Dumas, *Ann. de Chimie*, II. xliv.) In the last two cases the proportion of oxygen in the bases to that in the silica is very nearly as 1 : 4.

In the finer kinds of glass potash is always employed in preference to soda, because the glass made from soda, however carefully the materials are selected, has a bluish-green tinge, which is not observed when potash is used. The potash glass, however, is rather less brilliant than that which contains soda.

(498) *Glass consisting of Silicates of Soda and Lime.*—French plate glass and ordinary window glass are the most important varieties of this description. Plate glass is very fusible, although the oxygen of the bases which it contains amounts only to about one sixth of that of the silicic acid. Soda produces a more liquid and fusible compound than potash. The addition of lime to glass diminishes its fusibility whilst it increases its lustre and hardness without affecting the colour. Care must be taken not to employ an excess of lime, for it is liable to render the glass milky on cooling, although it may be perfectly transparent whilst hot.

Great care is required in the selection of the materials employed in the manufacture of the finer kinds of glass. The ingredients used in the plate glass of St. Gobain consist of 300 parts of white quartzose sand, 100 of dry carbonate of soda, 43 of lime, slaked by exposure to the air, and 300 of fragments of broken glass from previous meltings. The fuel employed in the furnace is wood.

These materials are intimately mixed, and then melted in a large, deep, conical crucible, in which, after they have been completely fused, they are allowed to stand at a high temperature for several hours, in order that the impurities may subside. Quantities of this mixture sufficient for casting a single sheet are then removed, by means of copper ladles, into a smaller square crucible, termed the *cuvette*.* When the glass is thoroughly melted the cuvette is removed from the furnace by a crane, and the glass is cast by pouring it upon a solid table of cast iron; along the edge of this table are ledges of metal, to regulate the thickness of the sheet of glass; the molten mass is immediately spread and formed into a plate by means of a heavy, hollow, metallic roller.

* In the Thames Plate-glass Works, the glass is melted in the same pot as that from which it is poured in casting. The pots are cylindrical, and not square, and the fuel employed is coal.

These sheets are next annealed by being placed in a heated oven, and allowed to cool very slowly down to the temperature of the air,—an operation which requires from a week to a fortnight for its completion. They are then levelled by cementing one plate with plaster of Paris upon a slab, and causing a second plate to move, by machinery, over the surface of the first, the grinding material being fine sand and water: a level surface having been thus obtained, it is smoothed by emery of gradually increasing fineness, and the final polish is given by friction with finely levigated colcothar, or peroxide of iron.

Window glass is made of a mixture of 100 parts of sand, with from 35 to 40 of chalk, 30 to 35 of soda ash, and from 50 to 150 of broken glass, or *cullet*. An equivalent amount of the cheaper sulphate of soda may be substituted in this mixture for the carbonate, for at a very elevated temperature the silicic expels the sulphuric acid; this decomposition may be facilitated by mixing the sulphate with about a tenth of its weight of charcoal; the sulphate is thus reduced to a lower state of oxidation, and the sulphur escapes in the form of sulphurous acid at a lower temperature than that required to expel the acid from the sulphate.

When carbonate of soda is used, the materials are first subjected to a heat insufficient completely to fuse the mass, and are *fritted* together, or heated until they agglomerate; moisture is thus completely expelled, and a part of the carbonic acid is got rid of: the frothing up of the mixture in the subsequent fusion, due to the expulsion of the carbonic acid, is also diminished, and the loss of alkali by volatilization is considerably lessened. The fritted mass is then transferred to other pots, and the temperature of the furnace is raised until complete fusion is effected. The mixture, after it has been thoroughly melted, is allowed to stand, in order that the bubbles of air may escape, and that the mass may become uniform in composition: the excess of sulphate of soda or of chloride of sodium which may have escaped decomposition rises to the surface and is skimmed off, forming what the manufacturer terms *glass-gall* or *sandiver*. The glass is then allowed to cool until it assumes the pasty, tenacious condition required for the manipulations of the glass-blower.

(499) *Silicates of Alumina, Lime, Iron, Magnesia, and Soda or Potash.*—The inferior descriptions of glass which are used for making wine bottles, carboys, and other articles in which a dark colour is unimportant, consist of a mixture of these silicates. The materials employed are of a coarser kind than those used in the preceding varieties of glass. A ferruginous or ochry sand, mixed

with soapmaker's waste, are common ingredients. Mr. Pellatt gives the following as a composition employed in making bottle glass:—Sand, 100 measures; soaper's waste, 80; gas lime, 80; common clay, 5; and rock salt, 3 measures. The ordinary English bottles are of an olive-green colour, produced by the presence of protoxide of iron: while some of the German bottles are of a pale brown, resulting from a mixture of the oxides of iron and manganese. Sometimes sulphate of baryta is added, with the view of rendering the glass more fusible. Bottle glass contains a smaller proportion of silica than any of the preceding varieties. One specimen, analysed by Dumas, presented a composition which would be approximatively represented by the formula, $6\ [(CaK)O,SiO_2] + (AlFe)_2O_3,\ 3\ SiO_2$; whilst in a second specimen the composition would be more nearly represented by $6[(CaK)O,SiO_2] + 2(AlFe)_2O_3,\ 3\ SiO_2$. The oxygen of the bases, in the first instance, is in the proportion to that of the silicic acid as 1 to 2, and in the second case nearly as 2 to 3.

(500) *Devitrification: Réaumur's Porcelain.*—Bottle glass is particularly liable to become devitrified by slow cooling, and to be converted into what is termed *Réaumur's porcelain.* In order to produce this effect, the glass may be imbedded in sand, or, still better, in a mixture of gypsum and sand, and heated up to a point sufficient to soften it, but just short of that required for its fusion. If it be now allowed to cool very slowly, it will be found to have entirely altered its aspect and properties; having become opaque and milk-white, and much resembling porcelain in appearance. It is now somewhat less fusible and less liable to crack on the application of sudden changes of temperature, and is much harder than the glass from which it was procured. It is a bad conductor of heat, but conducts electricity to a considerable extent, being comparable in this respect to marble (Pelouze). This alteration appears to be due to the partial separation of certain silicates, particularly of the silicates of lime and alumina, and their assumption of a more or less definite crystalline form. This crystallization is sometimes very beautifully and perfectly exhibited in the residues at the bottom of the glass pots, which are allowed to cool down with great slowness and regularity. Nodules of opaque radiated crystals are there often found surrounded by a transparent glass. A mass of these opaque crystals, analysed by Dumas, presented a composition which corresponded with the formula, $18[(CaNa)O,2\,SiO_2] + 2(Al_2O_3)\,9\,SiO_2$; whilst the transparent glass from which they had separated contained 3·5 per cent. less of silica, 1·4 less alumina, and a proportionately larger quantity of soda.

The devitrification of glass has been made the subject of experiment by Pelouze (*Chem. Gaz.*, Aug. 1855). He finds that the same sheet of glass may be devitrified, and again rendered transparent by fusion, many times in succession. Glass of any description may be devitrified, but the finer kinds of potash glass exhibit this phenomenon with difficulty. The throwing in of a small quantity of sand, or even of powdered glass, into a pot after it has cooled down to the viscid condition, greatly promotes the devitrification of the mass. The soluble soda glass of Fuchs, ($NaO, 4\,SiO_2$) is especially liable to devitrification from crystallization.

(501) *Silicates of Potash and Lead.*—The ordinary white glass in use in this country, commonly known as flint glass (the *cristal* of French writers), consists almost entirely of these silicates. Potash is used instead of soda in the preparation of flint glass, in order to avoid the bluish tint which is produced by soda in combination with oxide of lead. The oxide of lead imparts a greater degree of fusibility and density, as well as a high refractive and dispersive power; in consequence of which such glass, from its superior brilliancy, is better fitted for the manufacture of ornamental articles, and from its greater softness is more easily cut and polished. Lead glass has, however, the inconvenience of being readily scratched, and it is liable to tarnish and change colour, especially if the proportion of alkali be large. The alkalies corrode it slowly, and it becomes gradually blackened when left in contact with solutions of the sulphides. According to Faraday's experiments, English flint glass contains one third or more of its weight of oxide of lead; it may be represented very nearly by the formula ($KO, 3\,SiO_2 + PbO, 3\,SiO_2$). In a specimen from Newcastle, examined by Berthier, the proportion of silicate of lead was larger. This glass corresponded nearly to [$2(KO, 3\,SiO_2) + 3\,(PbO, 3\,SiO_2)$]. The composition of flint glass, however, is liable to considerable variation, even in different parts of the same pot, the lower portions having generally a greater density than those in the upper part of the pot. This arises from the density of the oxide of lead being much greater than that of the other materials, so that it is extremely difficult to preserve a uniform mixture. Faraday found, for example, that glass taken from the top of pots not more than six inches deep, might have a density of 3·28, while that from the bottom might have a density of 3·85: in one instance the glass at the top had a density of 3·81, that at the bottom of 4·75; and though these are extreme differences, there is no doubt that considerable variations occur in every pot of glass made in the usual way. This variation in the density

of the glass occasions great inconvenience in its application to the construction of optical instruments, owing to the difference of its refracting power in different portions of the same mass; and many endeavours have been made to overcome these defects. A lead glass of still higher refracting power was made by Guinand, in which the proportion of lead was very large, the formula being very nearly $[2(KO, 2SiO_2)+3(PbO, 2SiO_2)]$, the proportion of oxygen in the bases being to that in the silica as 1 to 4: its specific gravity was 3·61. Faraday (*Phil. Trans.*, 1830, p. 10) proposed, for a similar purpose, a compound of silicate and borate of lead, the density of which is 5·44: this glass has a pale lemon-yellow tint, and consists of $[3(PbO,SiO_2)+3PbO,BO_3]$. Of late years, a borosilicate of zinc has been introduced by Maez and Clemandot into the glass used for optical purposes, with considerable success.

Much of the success in the preparation of glass for optical purposes depends upon the selection of pure materials, and also on their complete incorporation. The plan which succeeds best in attaining the latter object was introduced by Guinand. After the fusion is complete, the melted glass is thoroughly stirred with a paddle of crucible clay; the crucible and its contents are then allowed to cool down slowly in the furnace; when cold, the pot is broken, and the mass of glass cut *horizontally* into slices, by which means pieces of uniform density may generally be obtained. A good optical glass may be made from a mixture of 100 parts of pure sand, 100 of minium, and 30 of refined pearlash.

The oxide of lead which is employed in the manufacture of flint glass is not ordinary litharge (758), but minium, or red lead (759), which is a higher oxide of lead, and is prepared with care from pure lead. The proportions of the materials usually employed in the manufacture of flint glass are, 300 of fine white sand, such as that from Lynn on the coast of Norfolk, or from Fontainbleau, 200 of minium, and 100 of refined pearlash, with about 30 parts of nitre. In all cases the selection of materials for the melting pot is of high importance. These pots are best made of an infusible clay, such as that from Stourbridge, which contains but little alumina and iron: 5 parts of clay and 1 part of ground burnt pots are trodden into a mass by the workman, and allowed to stand for three or four months: the mixture is then carefully wrought into pots about four inches thick, great care oeing taken to exclude air-bubbles. The pots are allowed to dry for several months in a warm room, after which they are removed to an annealing oven, where they are raised very gradually to the temperature of the furnace. Flint glass is always made in pots which

are arched over at top, and have an opening at the upper part of one side for the introduction of the charge and the withdrawal of the glass: they are set in the furnace in such a manner as to prevent the access of smoke and combustible gases to the interior, which would endanger the reduction of the oxide of lead to the metallic state. Plate glass, crown glass, and the other varieties of glass are made in open crucibles. The alumina, which is contained even in the finest glass, is chiefly derived from the action of the vitrified materials upon the clay of the pots.

(502) *Coloured Glasses.*—For the purpose of producing imitations of precious gems, a lead glass of still higher refracting power, termed *paste*, or *strass*, is employed, the proportion of oxide of lead exceeding 53 per cent.; the composition of this substance is very nearly represented by the formula ($KO, 2\,SiO_2 + 3\,PbO, 2\,SiO_2$); the proportion of oxygen in the bases being one fourth of that present in the silicic acid. A little borax is often added to this glass to increase its fusibility. Glass of this description, when properly cut, is employed to imitate the diamond. The yellow colour of topaz is given to the strass by the addition of about 1 per cent. of peroxide of iron, or by a mixture of 4 per cent. of oxide of antimony with a minute proportion (0·1 per cent.) of purple of Cassius. The brilliant blue of sapphire is imitated by means of a small quantity of oxide of cobalt.

It is, indeed, a property of glass to dissolve small quantities of many of the metallic oxides without losing its transparency; but the glass becomes coloured with more or less intensity, and with different hues, according to the nature of the metallic oxide employed. Protoxide of iron, even in small quantities, communicates colours which vary from a pale green to a deep bottle-green, according to the proportion in which it is present: sesquioxide of iron, on the contrary, has but feeble colouring power, unless present in considerable quantity, when it produces a yellow colour: protoxide of manganese is nearly colourless, but the sesquioxide communicates a violet tint to the glass. Advantage is taken of the knowledge of these facts in preparing colourless glass: protoxide of iron, in minute quantity, is a frequent impurity in the materials used, and it produces the green tinge often observed in ordinary glass: a minute quantity of black oxide of manganese corrects this, it imparts oxygen to the protoxide of iron, which thus becomes converted into the colourless peroxide, whilst the manganese itself being reduced to the state of protoxide exerts no injurious colouring effect. A little nitre or arsenious acid is sometimes added to glass instead of oxide of manganese, with a similar

effect in converting the protoxide of iron into sesquioxide. Oxide of chromium imparts an emerald-green tinge to glass; oxide of cobalt a deep blue. A mixture of the oxides of cobalt and manganese gives a black glass; black oxide of copper (CuO) produces a green; suboxide of copper (Cu_2O) an intense ruby red; whilst the sparkling appearance of avanturine is due to the dissemination of tetrahedral crystals of reduced metallic copper through the mass. Oxide of uranium communicates to the glass a peculiar opalescent yellow; different shades of yellow are also produced by oxides of silver and of antimony, and by finely divided charcoal; and a compound of gold with oxide of tin gives a magnificent ruby glass.

Sometimes glass is *flashed* or superficially coated with the coloured portion. A mass of colourless glass is in this case taken by the workman upon the end of his blowing tube, and then dipped into a pot of the coloured glass; on blowing out the lump of glass, a vessel is obtained the exterior layer of which is coloured, whilst the inner layer consists of colourless glass.

Painting on glass is effected by means of a very fusible glass, which when melted gives the required tint; this glass is reduced to a very fine powder, and worked up with turpentine into a pigment: it is then applied with a pencil to the surface of a sheet of ordinary glass. The painted glass is afterwards subjected to a heat which is sufficient to melt the coloured glass, but is not intense enough to soften the glass to which it is applied.

Enamel is the term given to an easily fusible glass, through which is disseminated some opaque white substance which is infusible at the temperature employed, such for example as the binoxide of tin: a metallic ash is prepared by calcining at a low red heat a mixture of 1 part of tin with from 1 to 6 parts of lead, in a flat cast-iron vessel; the ash so obtained is mixed with sand and alkali, the proportions of which may vary considerably. In one recipe for the preparation of enamel given by Knapp, the ashes of 4 parts of tin and 10 of lead are directed to be ground up with 10 parts of powdered quartz and 2 of pure soda ash. Other opaque bodies may be substituted for the oxide of tin in the preparation of enamel: in this manner bone ash, oxide of antimony, and even arsenious acid are sometimes employed to produce the opacity required. The enamel may be tinged of any colour by the suitable addition of metallic oxides. The enamel is applied with a brush to the surface to which it is to be attached, and is then fused by exposure to heat.

A modification of glass resembling enamel has been used to glaze cast-iron pots, as a substitute for tinning. It consists of

powdered flints ground with calcined borax, fine clay, and a little felspar. This mixture is made into a paste with water, and brushed over the pots, after they have been scoured with diluted sulphuric acid and well rinsed in water; while they are still moist, they are dusted over with a glaze composed of felspar, carbonate of soda, borax, and a little oxide of tin. Having been thus prepared, the pots are next carefully dried, and finally the glaze is fused or *fired* under a muffle at a bright red heat. Oxide of lead, though it increases the fusibility of the glaze, should be carefully avoided, for it does not resist the action of acids in culinary operations.

(503) *Properties of Glass.*—Well-made glass is unacted upon by any acid or mixture of acids except the hydrofluoric, which destroys it by combining with its silica. But it is not absolutely insoluble, though it is generally considered to be capable of withstanding the action of water. If glass be powdered and moistened with water, the liquid will dissolve a small quantity of alkali, sufficient to turn turmeric paper brown. Most varieties of powdered glass when exposed for some time to the air, were found by Pelouze to absorb carbonic acid in sufficient quantity to effervesce when treated with an acid, particularly if they had been kept moistened with water. If left long in water, or buried in moist earth, many kinds of glass become disintegrated slowly, and scale off in flakes which exhibit the brilliant colours of Newton's rings (110). This is particularly the case with the coarse glass used for wine bottles. Faraday found that some inferior kinds of bottle glass were destroyed rapidly by the action of diluted sulphuric acid.

At a high temperature water acts upon glass very rapidly; pieces of plate and window glass were suspended by Turner in the steam of a high pressure boiler, and in the course of four months, specimens of plate glass one fifth of an inch thick were completely decomposed; and Faraday found that flint glass, under similar circumstances, was still more rapidly acted upon.

If glass be suddenly cooled after fusion, it becomes extremely brittle. When drops of melted glass are allowed to fall into water, they solidify in pear-shaped masses, which may be subjected without breaking to considerable pressure, if gradually applied; but if the tail of one of these drops, known as *Rupert's drops*, be suddenly nipped off, the glass flies to pieces with a kind of explosion, and is shattered to powder. This effect appears to be due to the unequal tension to which the particles composing the drop are subjected, owing to the sudden cooling of the outer surface of the

glass, while the interior is still dilated: as the mass cools, the particles within, by adhesion to the external solid portion, are still kept in their dilated state; but a very slight disturbance of their relative position suffices to overcome their equilibrium, and when once the mass gives way at any one point, the cohesion of the whole is destroyed.

Similar changes occur if glass articles are allowed to cool suddenly by exposing them whilst red hot to the external air. Glass objects of various descriptions, if their surface be but scratched, or if they be brought suddenly from a cold room into a warm one, will often crack and fall to pieces. In order to prevent this mishap, it is necessary to subject the different articles, after they have received their destined shape at the hands of the workman, to the operation of annealing, which is a very slow and gradual process of cooling, by which the parts are enabled to assume their natural position with regard to each other. Even then, since glass dilates considerably on the application of heat, and is likewise a bad conductor, a sudden and incautious elevation of temperature, such as that occasioned by pouring boiling water into a cold glass, often determines its fracture. Care is required during the process of annealing, especially with the coarser kinds of glass, not to raise the temperature too high; as otherwise devitrification to a greater or less extent would be liable to ensue.

(504) CHARACTERS OF THE SALTS OF SODIUM.—We have no good direct tests for the salts of this metal, as it forms scarcely any insoluble compounds. Its most insoluble salt is what Fremy has termed the bimetantimoniate of soda (706), which is deposited in transparent octohedra when a solution of freshly prepared *bimetantimoniate of potash* is added to a neutral solution containing sodium, provided that the liquid has been previously freed from all bases except the alkalies: 1 part of sodium in 10,000 of water will produce a precipitate with this test after twenty-four hours. In analysis, a salt of sodium is concluded to be present when the absence of every other base has been proved, and yet a saline residue remains, which with bichloride of platinum gives yellow striated prismatic crystals ($NaCl, PtCl_2 + 6\ Aq$) by spontaneous evaporation. Andrews (*Chem. Gaz.*, x. 378) has pointed out a property of this salt which admits of its identification in extremely minute quantities; a drop of the solution suspected to contain sodium is mixed with a minute quantity of a solution of bichloride of platinum, and allowed to evaporate in a warm place; if before it is quite dry it be placed in the field of the microscope,

and examined by means of polarized light, minute crystals of the double chloride of sodium and platinum will be distinguished from the other salts by which they are accompanied, by their power of transmitting the polarized light, tinged with various colours, according to the thickness of the crystals. *Before the blowpipe* the salts of sodium are known by the intense yellow which they communicate to the outer flame, if a fragment be introduced at the point of the blue cone upon a loop of platinum wire.

The salts of sodium are in general more soluble than those of potassium; the sulphates of the two alkalies afford a striking instance of this difference: the sodium salts also often effloresce when exposed to the air, whilst those of potassium, on the other hand, frequently deliquesce, a fact well exemplified by the carbonates of the two bases.

§ III. Lithium (L=7). *Sp. Gr.* 0·5936.

(505) Lithium, the metallic base of the third of the alkalies, is of comparatively recent discovery, and derives its name from λίθος (a stone), as it has been found only in the mineral kingdom: it is but rarely met with. The minerals of most frequent occurrence which contain lithia are the three under-mentioned; they yield this alkali in proportion varying from 3 to 6 per cent. of their weight:—

Lepidolite, or lithia mica .	$2\,[(LK)\,Fl]+4\,(Al_2O_3, 3\,SiO_2)$
Triphane, or spodumene .	$3\,[(LNa)O, SiO_2]+4\,(Al_2O_3, 3\,SiO_2)$
Petalite	$3\,[(LNa)O, 2\,SiO_2]+4\,(Al_2O_3, 6\,SiO_2)$.

Metallic lithium is easily reduced from its chloride by means of an electric current obtained from four or six pairs of the nitric acid battery. The metal is of a white colour, and is fusible at 356°. It is harder than potassium, but softer than lead, and admits of being welded by pressure at ordinary temperatures; it can be drawn into wire, which, however, is inferior in tenacity to lead wire of the same dimensions. Lithium appears to be the lightest solid body known; it floats in naphtha, and has a density of only 0·5936. At high temperatures it is volatile, and may be distilled at a full red heat in a current of hydrogen. It cannot, however, be obtained by processes similar to those employed for potassium and sodium. A fragment of lithium burns upon a plate of mica with a very brilliant white light, emitting a heat sufficiently intense to melt a hole in the mica: when thrown upon water it swims and becomes oxidized, like sodium. If thrown into nitric acid it usually takes fire.

(506) *Lithia* (LO=15) **was discovered by Arfwedson, in 1818.**

It is extracted by carefully levigating the minerals that contain it, and igniting the fine powder with twice its weight of quicklime. The mass is treated with hydrochloric acid, then with sulphuric acid, and the sulphate of lithia is dissolved out from the sulphate of lime; the last traces of lime are removed from the solution of sulphate of lithia by oxalate of ammonia. This solution may then be deprived of sulphuric acid, and converted into caustic lithia by the addition of baryta water; the solution on evaporation yields hydrate of lithia.

Troost (*Ann. de Chimie*, III. li. 103) considers it to be more advantageous to melt 10 parts of powdered lepidolite with 10 of carbonate of baryta, 5 of sulphate of baryta, and 3 of sulphate of potash. The fused mass separates into two portions, a heavy transparent glass and a supernatant white slag; this white mass consists of a mixture of the sulphates of baryta, potash, and lithia, and contains nearly all the lithia. The sulphates of the alkalies are separated from the baryta by washing, and a portion of the sulphate of potash is removed by crystallization. The remaining sulphates of potash and lithia may be converted into chlorides by the addition of chloride of barium, and the two chlorides separated by evaporating to dryness and digesting them in a mixture of equal parts of alcohol and ether, which dissolves the chloride of lithium only.

Hydrate of lithia fuses easily below redness, and corrodes platinum vessels powerfully: silver capsules should therefore always be used in preparing it. This action upon platinum is one of the best indications of the presence of lithia. It appears to be due to the formation of an unstable *peroxide of lithium*, which imparts its oxygen rapidly to the platinum.

Chloride of Lithium ($LCl + 4\,Aq = 42{\cdot}5 + 36$) crystallizes in octohedra; it is one of the most deliquescent salts known. If its aqueous solution be evaporated at a high temperature, it loses a portion of its chlorine, whilst lithia is formed. Chloride of lithium is very soluble in alcohol, and in a mixture of equal parts of alcohol and ether.

Sulphate of Lithia ($LO,SO_3 + Aq = 55 + 9$) crystallizes in flat tables, which are very soluble in water. There appears to be no bisulphate of lithia, though a double sulphate of potash and lithia may be formed, consisting of $LO,SO_3 + 2\,(KO,SO_3)$.

Phosphate of Lithia ($3LO,PO_5 = 116$) is one of the most characteristic salts of this alkali: it is insoluble in water containing phosphates of the alkalies, and in alkaline solutions, but very soluble in acids even when very dilute. In order to prepare it, the insoluble metallic oxides and the earths, if present, are first precipitated, by

adding carbonate of soda to the solution, evaporating it to dryness, and treating the residue with boiling water: phosphate of soda is then added, and the whole evaporated to dryness; the residue is treated with boiling water, which removes the excess of the salts of soda, and leaves the phosphate of lithia. This salt fuses with carbonate of soda to a glass which is transparent while hot, but becomes opaque on cooling. The salt supposed by Berzelius to be a double phosphate of soda and lithia, appears to have been a mixture and not a definite compound.

Carbonate of Lithia ($LO,CO_2=37$) is only sparingly soluble in water, but is rather more soluble in a solution of carbonic acid; it has an alkaline reaction upon turmeric. At a dull red heat it melts into a white enamel, and by prolonged ignition loses a large portion of its carbonic acid.

CHARACTERS OF THE SALTS OF LITHIUM.—Generally speaking the salts of lithium are remarkably fusible; many of them are very deliquescent. They have a burning saline taste, and are distinguished by yielding a white precipitate of carbonate of lithia in cold concentrated solutions with *carbonate of potash*, but the precipitate disappears on adding water and applying heat; this reaction is less delicate when salts of ammonium are present. On the addition of *phosphate of soda* to solutions which are neutral or alkaline, the phosphate of lithia is formed; it is soluble in solutions of salts of ammonia. *Before the blowpipe* they communicate a purplish red colour to the flame, which is masked by the presence of soda in very small proportion; and when heated on platinum foil they corrode it rapidly.

§ IV. AMMONIUM, $H_4N=18$ (*Hypothetical*).

(507) *Action of Oxyacid Anhydrides on Ammonia.*—When dry gaseous ammonia (H_3N) is presented to the anhydrides of the oxyacids, such as sulphuric $(SO_3)_2$, sulphurous $(SO_2)_2$, or carbonic $(CO_2)_2$ anhydride, the gas enters into combination with the anhydride, and a peculiar compound is formed, in which it is maintained by Laurent and Gerhardt that one half of the ammonia only exists in the form of an ordinary ammoniacal salt, the other half having entered into combination with the elements of the anhydride, to form a compound termed an amidated acid (1047); the product obtained differs, therefore, in many important particulars from the compound which would be obtained by neutralizing with ammonia a solution of the same acid in water. In the latter case one of the ordinary 'salts of ammonia,' as they are usually

termed, is produced; in the former case an ammoniacal salt of a new amidated acid would be the result; but the preparation of these amidated compounds is difficult, and their true nature is not as yet thoroughly ascertained.*

The general properties of these bodies may be illustrated by examining the several combinations formed between the sulphuric and sulphurous anhydrides and dry ammoniacal gas.

(508) *Sulphuric Ammonide, Sulphatammon* (H_3N,SO_3).—When a current of dry ammoniacal gas is transmitted over sulphuric anhydride, placed in a flask, and maintained at a low temperature, taking care to leave the anhydride somewhat in excess, a hard gummy mass is produced, which when exposed to the air absorbs moisture and gradually deliquesces. The liquid thus obtained is saturated with carbonate of baryta, in order to remove the excess of acid, and is then evaporated; it yields large transparent crystals derived from an octohedron with a square base. This compound is the *parasulphatammon* of Rose, and consists, according to this chemist, of (H_3N,SO_3). It is freely soluble in water, but insoluble in alcohol. Its solution has a bitter taste, and gives no precipitate with salts of baryta, and none with bichloride of platinum. By long boiling with water, or with a solution of tartaric acid, it is slowly changed into ordinary sulphate of ammonia; but if heated with a free alkali, sulphate of ammonia is speedily produced, and ammonia is expelled.

If ammoniacal gas in excess be made to act upon sulphuric anhydride, another compound, isomeric with the former, termed *sulphatammon* by Rose, is obtained. It does not crystallize, and is quickly transformed when in solution into sulphate of ammonia.

A third compound, which may be procured in beautiful transparent crystals, is prepared by transmitting the vapour of sulphuric anhydride into ammoniacal gas in excess; the solid compound thus obtained is fused in a current of dry ammonia, and dissolved in water. The crystals obtained on evaporation, accord-

* These compounds of ammonia with the anhydrous acids are often incorrectly spoken of as *amides*. The amides of monobasic acids are, properly speaking, salts of ammonium which have been deprived of 2 atoms of water. Benzoate of ammonia ($H_4NO,C_{14}H_5O_3$), for example, when deprived of 2 atoms of water, furnishes a white fusible volatile solid, known as *benzamide* ($H_2N,C_{14}H_5O_2$). *Sulphamide* would be (H_2N,SO_2) and would contain an atom of water less than sulphuric ammonide. The ammonides, or ammons, contain only one atom of water less than the ordinary salts of ammonia. Sulphate of ammonia, for instance, may be represented as (H_4NO,SO_3), while sulphuric ammonide is (H_3N,SO_3). The different varieties of compounds obtained from the salts of ammonia by dehydration will be considered amongst the products of organic chemistry (1045 *et seq.*).

ing to Jacquelain, consist of $3\ H_3N, 4\ SO_3$. Although the solution of this compound has an acid reaction, it gives no precipitate with salts of baryta.

(509) *Sulphit Ammon* (H_3N,SO_2).—If dry sulphurous acid gas be mixed with an excess of perfectly dry ammoniacal gas, 2 volumes of the sulphurous anhydride and 4 of ammonia combine and form a yellow, amorphous, volatile, deliquescent compound, which when dissolved in water undergoes gradual decomposition.

If the sulphurous anhydride be in excess, a different compound is formed ($H_3N, 2\ SO_2$), corresponding in composition to bisulphite of ammonia from which 2 atoms of water have been abstracted: $H_3N,2\ SO_2 + 2\ HO = (H_4NO,HO, 2\ SO_2)$. It is a reddish-yellow, crystalline, volatile substance, freely soluble in water: when in solution, it is speedily decomposed into sulphate and trithionate of ammonia; $2(H_3N, 2\ SO_2) + 2\ HO = H_4NO,SO_3 + H_4NO,S_3O_5$. No such decomposition occurs when the ordinary bisulphite of ammonia is dissolved in water.

Anhydrous phosphoric and carbonic acids also form ammonides, which are analogous to those which have just been described.

(510) *Action of Anhydrous Hydracids on Ammonia.*—Dry ammoniacal gas likewise unites with facility with the anhydrous hydracids, but the compounds which are produced do not correspond in properties to the ammonides, but, on the contrary, form ordinary salts of ammonia. For example, dry hydrochloric acid and dry ammoniacal gases unite with avidity, and a white solid compound is produced, which is ordinary sal ammoniac; when dissolved in water it gives with solution of nitrate of silver the usual curdy precipitate indicative of chlorine, and with bichloride of platinum the usual yellow double salt characteristic of ammonia is deposited.

(511) *Theory of Ammonium.*—The differences between the characters of the compounds which dry ammonia forms with the oxyacid anhydrides, and those which it produces with the anhydrous hydracids were explained by Berzelius with the aid of a hypothesis originally suggested by Ampère, which has been termed the ammonium theory, by the adoption of which the salts of ammonia admit of being considered as exhibiting a composition analogous to that which exists in the case of the metallic salts.

According to this view, the compounds which are usually spoken of as salts of ammonia with the oxyacids do not contain ammonia at all, but a compound in which the elements of an atom of water have been added to those of ammonia, ($H_3N + HO$): in consequence of the assimilation of this atom of water, the sub-

stance which has united with the acid may be regarded as an oxide (H_4N,O), like oxide of potassium or oxide of lead, but which contains the compound body ammonium (H_4N), in the place of a metal. Anhydrous ammonia, when it unites with the oxyacid anhydrides, must therefore produce bodies very different from those obtained by the combination of hydrated ammonia with the same acids when hydrated, as may be seen, for instance, by comparing the formula of the compound with sulphuric acid in the two cases:—

$$\overbrace{H_3N,SO_3}^{\text{Sulphuric ammonide.}} \quad ; \quad \overbrace{H_4NO,SO_3}^{\text{Sulphate of ammonium.}}.$$

It is likewise easy to see why by the combination of anhydrous ammonia with a hydracid equally free from water, a true salt of ammonium should be formed: for instance, hydrochloric acid and ammonia by their union yield chloride of ammonium, a salt which obviously presents the closest analogy with the metallic chlorides; $H_3N+HCl=H_4N,Cl$.

With the oxyacids, then, ammonia forms two classes of compounds; the more important class constitutes the normal salts of the alkali in which the elements of water are necessarily present; the other class consists of the ammonides already described.

The theory of ammonium is supposed to derive considerable support from the following remarkable experiment:—If an amalgam of potassium or of sodium be moistened with a concentrated solution of sal ammoniac (H_4NCl), the amalgam immediately begins to increase in bulk, and ultimately swells up till it acquires 8 or 10 times its original volume, and it at the same time assumes a pasty consistence, but still preserves its metallic lustre. This substance, if exposed to a temperature of 0° F., crystallizes in cubes. It begins to undergo spontaneous decomposition immediately after its production, and the same effect occurs still more rapidly if it be placed in water: hydrogen gas is given off in minute bubbles, and ammonia is found in the solution. It is generally supposed that this remarkable amalgam consists of a combination of H_4N (or ammonium) with mercury. On attempting to expel the mercury by heat, however, the compound is decomposed, metallic mercury is sublimed, and a mixture of hydrogen and ammoniacal gas evolved: all other attempts to isolate the ammonium have been equally unsuccessful. The proportion of ammonium present in the amalgam, notwithstanding the great change in bulk and in properties experienced by the mercury, is extremely minute, amounting, according to Gay-Lussac and Thénard, to little more than $\frac{1}{1000}$th of the weight of mercury.

(512) *Solution of Ammonia.*—The preparation of ammoniacal gas and of its aqueous solution have been already described (311). The solution in water has an intensely alkaline reaction, and may be regarded as a solution of oxide of ammonium (H_4NO); but when heated, pure ammoniacal gas (H_3N) alone is expelled, and by passing the gas through a tube filled with quicklime to absorb the water which it carries over with it in suspension, ammonia may be obtained in a state of purity. The solution in water, when neutralized by acids and evaporated, yields salts of oxide of ammonium.

(513) SULPHIDES OF AMMONIUM.—Ammonium forms several sulphides which are freely soluble in water. The *protosulphide* (H_4NS), if it exist at all, cannot be procured in a solid form; it may be prepared in solution by dividing a quantity of solution of ammonia into two equal portions, through one of which sulphuretted hydrogen is transmitted as long as it is absorbed; the saturated liquid is then added to the second portion of the solution. It is however possible that the two solutions H_4NS,HS, and H_3N,HO may remain uncombined instead of uniting to form $2\ H_4NS+HO$. This liquid dissolves many of the sulphides of the metals which furnish acids with oxygen, and forms double sulphides with them (442). Many of these double sulphides may be obtained in crystals; this, for example, is the case with those which contain the pentasulphide of antimony and of arsenic, and the tersulphide of molybdenum.

Bisulphide of Ammonium (H_4NS_2) may be obtained in large yellow, transparent, very deliquescent crystals, by passing sulphur and dry ammonia through a red-hot porcelain tube. In the hydrated form it has been long known as *Boyle's fuming liquor*, and is prepared by calcining 3 parts of slaked lime with 2 of sulphur, and distilling 3 parts of this mixture with 2 of sal ammoniac and 1 part of sulphur; a yellow, oily, fœtid liquor passes over, which fumes in the air, and on cooling deposits deliquescent, yellow, lamellar crystals; acids disengage hydrosulphuric acid from it, and cause a deposit of sulphur. Its aqueous solution dissolves a large quantity of sulphur, forming a *pentasulphide*, H_4NS_5, which crystallizes from its solution in long orange-yellow oblique rhombic prisms.

Hydrosulphate of Sulphide of Ammonium ($H_4NS,HS=51$) is the liquid commonly used as a reagent under the name of hydrosulphate of ammonia: it is formed by transmitting sulphuretted hydrogen through a solution of ammonia to saturation. This liquid when newly formed is colourless, but it absorbs oxygen

rapidly from the air, and becomes yellow from formation of bisulphide of ammonium, whilst a hyposulphite of ammonia is produced in the liquid; $2\ (H_4NS,HS)+O_5=H_4NS_2+H_4NO,S_2O_2+2\ HO$. The solution of this substance dissolves the sulphides of the electro-negative metals as readily as the protosulphide of ammonium does, but sulphuretted hydrogen is liberated from the hydrosulphate, for example; $3\ (H_4NS,HS)+AsS_5$ become $3\ H_4NS,AsS_5+3\ HS$. Hydrosulphate of ammonia (H_4NS,HS) may be obtained in the anhydrous form, by mixing dry sulphuretted hydrogen with dry ammoniacal gas; 4 volumes of ammonia combine with 4 volumes of sulphuretted hydrogen, and condense in yellowish, transparent, brilliant plates, which are very volatile, and sublime without decomposition; they are very soluble in water.

(514) Chloride of Ammonium ($H_4N,Cl=53{\cdot}5$); *Sp. Gr.* 1·578.—*Muriate of Ammonia*, or *Sal Ammoniac* as it is commonly termed, is the most important of the salts of ammonium. It may be formed directly by the union of hydrochloric acid and ammoniacal gases: it was formerly imported from Egypt in considerable quantity as a product of the distillation of dried camel's dung, but in this country it is now furnished almost entirely from *ammoniacal liquor*, a waste product from the coal-gas works. Coal contains a portion of nitrogen, which, during the process of distillation, is partially converted into ammonia; this combines with carbonic acid and with sulphuretted hydrogen: these compounds are condensed with the gas liquor from which the ammonia is subsequently extracted. The best process for preparing sal ammoniac consists in neutralizing the gas liquor with hydrochloric acid. For this purpose the liquid is pumped up from the tank into the decomposer, a large wooden vat closely fitted with a cover, connected with flues for carrying off the gaseous products; the acid in suitable quantity is placed in jars, from which it is slowly drawn off by siphons, and is thus allowed to mix gradually with the liquor; abundance of gas is disengaged, and is made to pass through a fire, where the hydrosulphuric acid is burned: much of the tarry matter (derived from the coal) which was held in solution, is deposited during this operation, and the liquid froths up considerably, any loss which might be thus occasioned being prevented by the use of a waste pipe, by which the overflow is carried back into the well below. When the liquor has thus been neutralized, it is run into a covered evaporating pan, where the remaining portions of sulphuretted hydrogen are expelled; after further concentration it is drawn off into shallow wooden vessels, lined with lead, to crystallize: the crystals thus procured are drained, and the mother-liquor

is again concentrated. The rough crystals are next heated in a cast-iron pan, to a point approaching that at which sublimation commences; a good deal of tarry matter, which the salt still retains, is expelled during this roasting. The salt is then sublimed in a strong cylindrical iron pot, furnished with a leaden or iron cover lined with fire-clay; the fire underneath is gradually raised, and the salt sublimes and is deposited in large dome-shaped cakes on the inner surface of the cover.

The liquors which are condensed during the distillation of bones in closed iron cylinders, in the process of preparing animal charcoal, are highly charged with an impure carbonate of ammonia, contaminated with volatile, oily, and tarry matters derived from the action of heat upon animal matter: these liquors furnish a source of ammoniacal salts of some importance: formerly this liquid, after being subjected to a partial purification, was commonly known as *spirit of hart's-horn*, because a similar liquor was originally obtained by the distillation of horn shavings.

Sublimed muriate of ammonia forms semi-transparent, tough, fibrous masses. 100 parts of the salt contain 68·22 of hydrochloric acid, and 31·78 of ammonia. It is very soluble in water, 100 parts of which at 60° dissolve 36 parts, and at the boiling point, 88·9 parts of the salt: a great reduction of temperature occurs whilst it is undergoing solution, and it is hence employed as a common ingredient in freezing mixtures; it crystallizes usually in an arborescent form, but sometimes in cubes and octohedra. Muriate of ammonia has a sharp, acrid taste; it is slightly soluble in alcohol. When heated, it sublimes much below redness, before undergoing fusion. It has a strong tendency to form double salts with the chlorides more electro-negative than itself. The compounds of many metals which form volatile chlorides, such as the arseniates and arsenites, the antimoniates, and the stannates, when heated with muriate of ammonia, lose the arsenic, antimony, and tin in the form of chlorides of these metals; and the salts of lead, iron, zinc, and alumina, are decomposed and completely volatilized when ignited with a large excess of muriate of ammonia. Rose observed that all the basic protoxides of the form MO, such as protoxides of iron, cobalt, and manganese,—and oxides of the form M_2O, such as suboxide of copper, also decompose muriate of ammonia, when heated with its solution, the ammonia being displaced by the metallic oxide, and a fixed metallic chloride being formed, whilst not one of the sesquioxides has this power.

(515) SULPHATE OF AMMONIA ($H_4NO,SO_3=66$; *Sp. Gr.* 1·750) is prepared in large quantity by neutralizing gas liquor with sul-

phuric acid; but it may be obtained in a pure form by adding sesquicarbonate of ammonia to the acid so long as any effervescence ensues. It crystallizes in flattened prisms, which are isomorphous with those of sulphate of potash; it is soluble in twice its weight of cold water, and has a sharp disagreeable taste; when heated, it decrepitates, melts, and undergoes partial decomposition, sulphite of ammonia being among the products. It forms a great number of double salts isomorphous with the corresponding salts of potash. Sulphate of ammonia has lately been applied to muslins and other fabrics for the purpose of preventing them from burning with flame in case they should accidentally take fire. The finished goods are dipped into a solution containing 10 per cent. of the crystallized salt, and dried in a centrifugal machine, or *hydro-extractor*.

An *acid sulphate* may be formed which has the formula ($3\ H_4NO,HO,4\ SO_3$), and a *double sulphate of soda and ammonia* ($H_4NO,NaO,2\ SO_3+4\ Aq$) may be readily formed by mixing solutions of the two salts, and evaporating the liquid till it begins to crystallize.

(515 *a*) NITRATE OF AMMONIA (H_4NO,NO_5)=80; *Sp. Gr.* 1·635.—This is a salt of some importance to the chemist, as it furnishes him with a ready source of pure protoxide of nitrogen. It is procured by neutralizing nitric acid with a solution of sesquicarbonate of ammonia: on evaporation, the salt crystallizes in long striated anhydrous prisms; by rapid evaporation it is obtained either in a fibrous or in an amorphous mass. It has a bitter acrid taste, is somewhat deliquescent, and during the act of solution causes a great depression of temperature, hence it is often used in frigorific mixtures: when heated to 392° it melts, and at 480° it undergoes complete decomposition, being converted into protoxide of nitrogen and water, in the manner already described (306); $H_4NO,NO_5=2\ NO+4HO$. If thrown on a red-hot plate it melts, hisses, and is dispersed with a faint bluish flame.

(516) CARBONATES OF AMMONIA.—There are several compounds of ammonia with carbonic acid. The most important of these is the *sesquicarbonate* ($2\ H_4NO,3\ CO_2=118$), the common carbonate or *smelling-salts* of the shops. It is usually obtained as a semitransparent fibrous mass, by mixing chalk with half its weight of sulphate, or of muriate, of ammonia, collecting in leaden vessels the crude product which comes over on applying heat, and resubliming the mixture at a temperature of about 150°; the salt is received in leaden hoods, in the interior of which it is deposited. During this process a large quantity of free ammonia escapes, because the neutral carbonate of ammonia cannot exist at that temperature.

The decomposition of the muriate of ammonia may be represented thus:—

$$3\ (H_4N,Cl) + 3\ (CaO,CO_2) = 3\ CaCl + 2\ H_4NO,\ 3\ CO_2 + H_3N + HO.$$

The sesquicarbonate of ammonia has a strong, pungent smell, like that of pure ammonia, arising from the continual volatilization of the neutral carbonate at ordinary temperatures: $2\ H_4NO,\ 3\ CO_2$ becoming $H_4NO,HO,\ 2\ CO_2 + H_3N,CO_2$. Owing to this loss of carbonate the salt speedily becomes coated with a white, spongy crust of bicarbonate. It has an acrid taste and a strongly alkaline reaction. 100 parts of the freshly sublimed salt contain 28·81 of ammonia, 55·93 of carbonic acid, and 15·26 of water. Its aqueous solution, if saturated and exposed to a temperature of 32°, deposits large, transparent, octohedra with a rhombic base ($2\ H_4NO,\ HO,\ 3\ CO_2 + 2\ Aq$). According to the researches of Rose there are several compounds resulting from the combination of carbonate of ammonia with different proportions of bicarbonate of ammonia.

The *Bicarbonate of Ammonia* ($HO,H_4NO,\ 2\ CO_2 = 79$; *Sp. Gr.* 1·586) is isomorphous with the corresponding potash salt; it is soluble in 8 parts of cold water, and if the solution be heated, carbonic acid escapes; when exposed to the air the dry salt becomes slowly volatilized. It may be obtained in large transparent prismatic crystals, derived from a rhombic octohedron [$2\ (HO,H_4NO,\ 2\ CO_2) + Aq$], by pouring boiling water upon the sesquicarbonate, corking the flask, and allowing it to cool. It is sometimes formed spontaneously during the decomposition of guano, and is then deposited in large regularly formed crystals.

Carbonate of ammonia combines with many metallic carbonates, forming double salts.

(517) Phosphates of Ammonia, corresponding to those of soda, may be formed; but the only one of any importance is the tribasic phosphate of soda, oxide of ammonium, and water, known as *microcosmic salt* ($NaO,H_4NO,HO,PO_5 + 8\ Aq = 137 + 72$). It is prepared by mixing a hot solution of 6 parts of phosphate of soda with a solution of 1 part of muriate of ammonia in the smallest possible quantity of water; common salt remains in solution, and the phosphate crystallizes in large transparent prisms, which are efflorescent in a dry air. It may be purified by a second crystallization from a small quantity of hot water to which a little free ammonia has been added to compensate for the loss of ammonia which the salt sustains when heated in solution. By ignition, all the oxide of ammonium and water are expelled, metaphosphate of soda remains, and fuses into a colourless glass

at a red heat. This salt is sometimes employed as a flux for experiments with the blowpipe, as the glass dissolves many metallic oxides, and forms transparent beads, from the colour of which the presence of certain metals, in many cases, can be ascertained.

(518) *Ammoniated Salts.*—Anhydrous ammonia enters into combination with many anhydrous metallic salts in a manner somewhat analogous to that of water of crystallization. In other cases, salts which usually retain water of crystallization lose it either partially or entirely when they combine with ammonia, but the number of equivalents of ammonia is not influenced by the proportion of water with which the salt generally unites. Chloride of silver, of tin, of copper, and of calcium, sulphate of copper and of zinc, nitrate of silver and of copper, form compounds of this kind with ammonia. The composition of some of these salts is exhibited in the subjoined table:—

		Eq.	Sp. Gr.
Ammoniated chloride of silver	$AgCl+2\,H_3N$	177·5	
1. Ammoniated chloride of copper	$CuCl+3\,H_3N$	118	
2. Ammoniated chloride of copper	$CuCl+2\,H_3N,HO$	110·5	1·671
3. Ammoniated chloride of copper	$CuCl+H_3N$	84	2·194
Ammoniated chloride of tin	$SnCl+H_3N$	110	
Ammoniated chloride of calcium	$CaCl+4\,H_3N$	123·5	
Ammoniated sulphate of silver	$AgO,SO_3+2\,H_3N$	190	2·918
Ammoniated sulphate of copper	$CuO,SO_3+2\,H_3N,HO$	122·5	1·790
Ammoniated nitrate of silver	$AgO,NO_5+2\,H_3N$	200	
Ammoniated nitrate of copper	$CuO,NO_5+2\,H_3N$	127·5	1·874

These compounds when exposed to the air lose a portion of the ammonia; if heat be applied, the ammonia is often entirely expelled, as in the case of ammoniated chloride of silver, the compound originally employed by Faraday for obtaining ammoniacal gas in the liquid form (182). The chloride of silver is left unaltered when the ammonia is expelled. In other instances the elements of ammonia react upon the salt and decompose it. Ammoniated chloride of copper, $CuCl, 3\,H_3N$, when heated, first loses 2 atoms of ammonia, and then the residue $(CuCl, H_3N)$ undergoes the following decomposition; $6\,(CuCl,H_3N) = 3\,Cu_2Cl + 3\,H_4NCl + 2\,H_3N + N$. The corresponding compound of nickel is reduced to the metallic state when heated.

In solution ammonia also combines with many metallic salts, forming analogous compounds: by exposure to air the ammonia escapes. Salts of zinc form a colourless solution with excess of ammonia; those of cobalt give a pink, which passes into green; whilst the salts of nickel and of copper give a violet blue solution.

(519) *Action of Ammonia upon Salts in Solution.*—From what

has been already stated it is evident that ammonia acts upon metallic salts not merely as a powerful base, as in cases where potash or soda are made to act upon them. The results produced by the addition of ammonia to a solution of a metallic salt may be stated as follows;—

1. If the ammonia be insufficient in quantity to neutralize the whole of the acid contained in the metallic salt, a sparingly soluble subsalt of the metal may be precipitated: in this way subsulphate of copper, subnitrate of lead, or subsulphate of alumina, may be formed; for instance, $4\ (CuO,\ SO_3) + 3\ H_3N + 7\ HO = 3\ (H_4NO,\ SO_3) + (4\ CuO,\ SO_3 + 4\ Aq)$.

2. If the ammonia be present in excess, it may combine directly with the acid of the salt, and produce with it a soluble salt of ammonia, whilst a precipitate of the metallic oxide in a hydrated form is occasioned; as when alumina, oxide of chromium, or peroxide of iron, is thrown down from its salts:—for example,

$$2\ (Fe_2O_3,\ 3\ SO_3) + 6\ H_3N + 9\ HO = 6\ (H_4NO,SO_3) + 2\ Fe_2O_3,\ 3\ HO.$$

3. Sometimes the ammonia, if in excess, combines with the precipitated oxide, as it does with peroxide of uranium, when mixed with solution of pernitrate of uranium:—

$$U_2O_3,\ NO_5 + 2\ H_3N + 2\ HO = (H_4NO,NO_5) + (H_4NO,U_2O_3).$$

4. In other cases a double salt of ammonia and the base may be precipitated, as when ammonia is mixed with a solution containing phosphoric acid and magnesia, in which case a double phosphate of magnesia and ammonia is formed and deposited in crystals: $2\ (MgO,\ SO_3) + 3\ H_4NO,PO_5 = 2\ (H_4NO,\ SO_3) + (H_4NO,\ 2\ MgO,PO_5)$.

Reactions corresponding to the four modes of action just indicated frequently occur, when a fixed alkali, such as potash or soda, is mixed with a metallic salt.

5. A soluble compound may be formed, into the composition of which both the metallic oxide and the ammonia enter, and unite with the acid so as to form a species of double subsalt. Hydrate of magnesia, hydrated oxide of copper, of zinc, of cobalt, or of nickel, when free from acid, are very sparingly dissolved by a solution of pure caustic ammonia, but a mixture of chloride of ammonium, or even of carbonate of ammonia, with caustic ammonia, dissolves them without difficulty. The compounds thus procured are definite in composition, and similar in nature to those enumerated in the table given in the preceding page as the result of the action of ammoniacal gas upon the dry salts of the metals. The solutions of these salts in ammonia frequently absorb oxygen

rapidly if exposed to the air: salts of iron, manganese, and cobalt furnish examples of this kind.

6. But it occasionally happens that the elements of ammonia enter into the composition of the salt in a more intimate manner. When a solution of corrosive sublimate (HgCl) is mixed with a solution of potash, a yellow precipitate of oxide of mercury is formed, and chloride of potassium remains in solution; $HgCl + KO, HO = HgO + KCl + HO$; but the case is otherwise if ammonia be added; a white precipitate is then formed, the composition of which is unchanged by the addition of an excess of ammonia. Kane (*Phil. Mag.*, June, 1836, p. 495) showed that this body has a composition which may be represented by the formula of $HgCl,HgH_2N$. Its formation may be explained by the following equation:—

$$2\,HgCl + 2\,H_3N = (HgCl,HgH_2N) + H_4NCl.$$

From this result, conjoined with others obtained from an examination of other ammoniacal derivatives from copper, palladium, and other metals, Kane was led to believe that ammonia is not a direct compound of hydrogen with nitrogen, but rather a combination of an atom of amidogen with one of hydrogen; so that he represents ammonia as HAd (Ad standing for amidogen, H_2N); the atom of hydrogen being liable to displacement by an equivalent either of mercury or of certain other metals. One atom of such an amide of mercury (HgAd) is, according to Kane, contained in white precipitate, in combination with 1 atom of chloride of mercury.

Later experiments, however, especially those of Hofmann, on the formation of bases by substitution from ammonia, have not strengthened the theory proposed by Kane; they have shown that not only does 1 atom of hydrogen admit of being displaced by some equivalent substance, but that each of the 3 atoms of hydrogen in ammonia admits of being thus displaced; nay more, that bodies may be obtained which are derived from ammonium, in which all the 4 atoms of hydrogen in this compound have been displaced by other equivalent bodies. These investigations point rather to the view that white precipitate is a body corresponding in composition to chloride of ammonium (H_4N,Cl) but in which 2 atoms of hydrogen are displaced by 2 atoms of mercury (Hg_2H_2N,Cl). We shall recur to these investigations when considering the properties of the organic bases (1027).

7. Within the last few years several remarkable bases which are derived from ammonia have been formed, but into the composition of which certain metals enter. Although these compounds contain the elements of ammonia, and of the oxides of the metals, yet they do

not, by means of the ordinary tests, give any indications either of ammonia or of the metals which enter into their composition.

In this manner several series of compounds have been procured, some of which contain platinum, others contain cobalt, and others palladium; in most instances they form crystallizable and well characterized salts.

Amongst the compounds thus formed, four of those obtained from platinum may be selected by way of illustration. The first of these contains a base for which Gerhardt has proposed the name of *platosamine*, PtH_3NO; the second, he has termed *diplatosamine*, $PtH_6N_2O + Aq$; the third, *platinamine*, $PtH_3NO_2 + 2\ Aq$; and the fourth, *diplatinamine*, $PtH_6N_2O_2$. The base last mentioned has not as yet been obtained in a separate form.

Each of these bases forms with hydrochloric acid a crystallizable salt, the composition of which is represented by the empirical formula given in the second column of the following table, whilst the third column shows the relation of the compound to the chloride of platinum from which it is obtained; the first two compounds being derived from the protochloride of platinum, the last two being formed from the bichloride of platinum:—

Chloride of platosamine . .	$PtH_3N\,Cl$	or	$PtCl,\ H_3N$
Chloride of diplatosamine .	PtH_6N_2Cl	or	$PtCl,\ 2\,H_3N$
Chloride of platinamine . .	$PtH_3N\,Cl_2$	or	$PtCl_2,\ H_3N$
Chloride of diplatinamine .	$PtH_6N_2Cl_2$	or	$PtCl_2, 2\,H_3N$.

(520) CHARACTERS OF THE COMPOUNDS OF AMMONIUM.—The salts of ammonium are colourless; they are all decomposed by heat, unless the acid itself be capable of volatilization, in which case they may generally be sublimed without change. They are distinguished from the salts of all the metals, with the exception of the alkaline bases, by the absence of any precipitate when their solutions are mixed with a solution of carbonate of potash or of soda.

The salts of ammonium may be recognised by heating them in the solid form with *quicklime* or with *caustic potash*, when pungent fumes of ammonia are extricated: if their solutions be boiled with either potash or lime a similar extrication of ammonia ensues, and if the quantity of ammonia be too small to be detected by the smell, a rod dipped into *hydrochloric acid* diluted with an equal bulk of water, produces white fumes when brought into the vapour; these fumes are due to the production of sal ammoniac, which is formed by the union of the gaseous ammonia with the vapour of the hydrochloric acid, and is precipitated in the solid form. A

characteristic test of free ammonia is the formation of the black iodide of nitrogen in a solution of iodine in iodide of potassium; but if the proportion of ammonia be very minute the only perceptible change is the disappearance of the brown colour of the solution.

Another very characteristic and extremely delicate test of ammonia and of its salts is the following:—Prepare a solution of corrosive sublimate to which iodide of potassium is added until the precipitate of iodide of mercury is nearly redissolved; then pour into the clear liquid a solution of caustic potash, and allow it to become perfectly clear by standing. If this solution be added in excess to a liquid containing a trace of ammonia, or of its salts, it assumes a brown tinge, or furnishes a brown precipitate, according as the proportion of ammonia is less or more, iodide of tetrhydrargammonium, or ammonium in which 4 atoms of hydrogen are displaced by 4 of mercury ($Hg_4N,I + 2\ HO$) being formed (Nessler). The reaction does not occur in the presence of sulphides or cyanides of the metals of the alkalies.

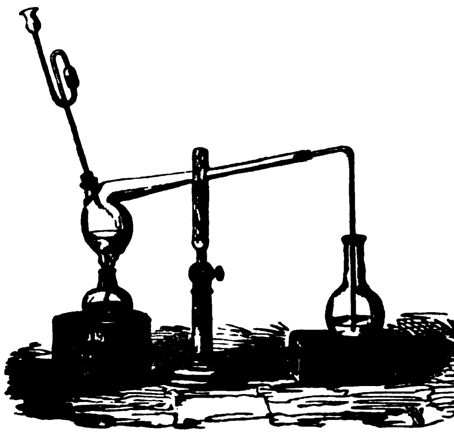
The Phosphomolybdate of Soda is also a very delicate test for the presence of a salt of ammonium in solution. The mode of preparing and applying it is described under the head of molybdic acid (692). Another still more delicate test of the presence of free ammonia is afforded by the use of a liquid consisting of a mixture of equal parts of a saturated solution of arsenious acid and of a solution of nitrate of silver containing 10 grains to the ounce; traces of ammonia cause the formation of the yellow arsenite of silver (Dr. A. Taylor). This, however, though a sensitive is not a characteristic test, since a trace of any free alkali or alkaline earth produces a similar result.

(521) *Estimation of Ammonia.*—The most accurate method of determining the quantity of ammonia in any substance, if the absence of potash has been ascertained, consists in precipitating it by the *bichloride of platinum*, observing all the precautions mentioned when speaking of the use of this test with potash; a yellow insoluble double salt falls, consisting of $PtCl_2,H_4NCl$: it contains, in 100 parts, 7·65 of ammonia. This salt is easily distinguished from the corresponding compound of potassium, by heating it to redness, in which case metallic platinum alone remains; whereas the potassium salt, though decomposed by this treatment, leaves the platinum mixed with chloride of potassium, which may be dissolved out of the residue.

(522) The following method of determining the amount of ammonia in guano or in crude ammoniacal salts will often be found

useful. One hundred grains of the matter for trial are placed in a small retort, fig. 317, and two ounces of water are added: by means of a bent funnel half an ounce of a solution of potash, of specific gravity 1·25, is also introduced; about an ounce and a half of liquid is gradually distilled into the flask, which contains a measure of 1000 water grains of sulphuric acid (one burette full, fig. 312) diluted to the strength required for the determination of soda for alkalimetrical purposes (480). If the mixture froths up inconveniently when boiled, milk of lime may be substituted for the solution of potash. As soon as about an ounce and a half of liquid has been distilled, the contents of the retort are allowed to cool a little, and another ounce of water is introduced into the retort by the funnel; a second distillation is then proceeded with, until the quantity of water just added has passed over; an ounce more of water is added to the contents of the retort, and the distillation is renewed a third time until this additional quantity of water has passed over: the liquid in the flask is then decanted into an evaporating basin; the flask twice rinsed out with a small quantity of distilled water, and the washings are added to the acid liquid. This is now to be neutralized in the usual way, by means of a standard solution of soda; the soda solution being of such a strength that one measure of it exactly neutralizes an equal measure of the acid liquid originally introduced into the flask. Suppose that this liquid from the flask now requires 67 measures of soda solution instead of 100; 33 measures of the acid will have been neutralized by the ammonia; a quantity of ammonia will therefore have passed over equivalent to 33 grains of soda. The corresponding quantity of ammonia may be calculated from the equivalent numbers of the two alkalies:—

FIG. 317.



$$\text{Thus, } \overset{\text{Eq. NaO.}}{31} : \overset{\text{Eq. H}_3\text{N.}}{17} :: 33 : 18{\cdot}09$$

100 grains of the material operated on in this case would therefore have contained 18·09 grains, or 18·09 per cent of ammonia.

CHAPTER XII.

GROUP II.—METALS OF THE ALKALINE EARTHS.

§ I. BARIUM ($Ba=68{\cdot}5$).

(523) BARIUM occurs abundantly under the form of sulphate of baryta, and is not unfrequently found as carbonate of baryta. Davy first procured it in the metallic state by making mercury the platinode of a voltaic battery in a strong solution of hydrate of baryta; the barium was thus obtained as an amalgam, from which the mercury was expelled by heating it strongly in a green glass tube filled with hydrogen; but it does not appear to have been thus obtained in a state of purity. When procured by the voltaic decomposition of its fused anhydrous chloride, it is of a pale yellow colour; but it is not easily obtained in distinct beads. Barium decomposes water rapidly at ordinary temperatures. In the air it is quickly tarnished by absorbing oxygen. It decomposes glass at a red heat.

(524) COMPOUNDS OF BARIUM WITH OXYGEN.—Baryta forms two oxides, a protoxide, BaO, and a peroxide, BaO_2: the first is the only one which forms salts.

Baryta ($BaO=76{\cdot}5$); *Sp. Gr.* 5·456.—Anhydrous baryta may be obtained by exposing the nitrate to a red heat in a capacious porcelain crucible; the salt decrepitates, melts, and then boils up and gives off a large quantity of oxygen mixed with nitrogen, leaving the baryta as a grey, porous mass, which absorbs moisture and carbonic acid if exposed to the air. If mixed with one eighth of its weight of water it slakes, forming a hydrate, with extrication of great heat. Baryta may be fused before the oxyhydrogen blowpipe.

The sulphide of barium may be employed for procuring pure *hydrate of baryta*, by boiling its solution with oxide of copper: hyposulphite of baryta and disulphide of copper, both of which are insoluble, are produced, and hydrate of baryta is dissolved; $6\,BaS + 8\,CuO = 5\,BaO + BaO,S_2O_2 + 4\,Cu_2S$: the hot liquid is filtered, and crystals of the hydrate ($BaO,HO + 8\,Aq$; Bloxam) are deposited as the solution cools. Crystals of hydrate of baryta may also be obtained by adding to a boiling solution of caustic soda, of sp. gr. 1·12, an equivalent quantity of nitrate of baryta in small quantities at a time. The hot solution is filtered into a vessel covered from the air, and the hydrate is deposited as the liquid cools. The crystals are soluble in 3 times their weight of boiling water, and in 20 of cold

water; the liquid has a strongly alkaline reaction. When exposed to the air both the crystals and the solution absorb carbonic acid; by heat 8 equivalents of water are expelled from the crystals, and a monohydrate is left, of *Sp. Gr.* 4·495; it fuses at a heat above redness, and retains its water at all temperatures. Hydrate of baryta is sparingly soluble in alcohol.

Peroxide of Barium ($BaO_2 = 84·5$) is formed by passing oxygen over anhydrous baryta at a low red heat; or by mixing pure baryta with an equal weight of chlorate of potash and heating to low redness; in the latter case ignition commences at one point, and spreads through the mass like tinder; $6\,BaO + KO,ClO_5 = KCl + 6\,BaO_2$: the chloride of potassium may be dissolved out by water, and a bulky, white, hydrated peroxide of barium ($BaO_2 + 6\,Aq$), insoluble in water, remains. By strong ignition the peroxide of barium again parts with its oxygen. Boussingault (*Ann. de Chimie*, III. xxxv. 5) even proposed to make use of caustic baryta as a means of preparing oxygen on a large scale by alternately passing atmospheric air over the baryta, raised to a dull red heat, and then expelling the absorbed oxygen by intense ignition: the presence of a small quantity of aqueous vapour greatly assists the expulsion of the oxygen, but the process cannot be worked with facility. The anhydrous peroxide combines with water when moistened, without evolving any sensible amount of heat, and crumbles down to a white powder: it is used for procuring the binoxide of hydrogen. Peroxide of barium becomes white hot when heated over a spirit lamp in a rapid current of carbonic, or of sulphurous acid; small white flames burst out from its surface, whilst carbonate or sulphate of baryta is formed.

(525) Sulphides of Barium.—Of these the most important is the *protosulphide* ($BaS = 84·5$). The preparation of this substance from the native sulphate of baryta presents some interest to the chemist, for it enables him to obtain with ease the soluble salts of baryta from its insoluble sulphate. In order to prepare the sulphide, either the native or the artificial sulphate is reduced to a very fine powder, and intimately mixed with an equal weight of starch or flour or with one-tenth of its weight of powdered charcoal, made up into a paste with oil, and introduced into a crucible lined with charcoal: the cover is luted on, and the crucible and its contents are exposed for an hour to an intense heat. By this treatment the sulphate of baryta is deoxidized, carbonic oxide escaping, whilst sulphide of barium remains: $BaO,SO_3 + 4\,C = BaS + 4\,CO$. When the mass thus obtained is treated with successive small quantities of boiling water, the sulphide is decom-

posed; the first portions of the solution have a yellow colour, owing to the formation of hydrosulphate of the sulphide of barium, which absorbs oxygen and becomes partially converted into bisulphide of barium, whilst the later washings contain gradually increasing quantities of hydrate of baryta; $2\ BaS + 2\ HO = BaS,HS + BaO,HO$, and $BaS,HS + O = BaS_2 + HO$; but if the mass be treated with a sufficient quantity of boiling water, it becomes entirely dissolved, and the sulphide is deposited as the solution cools in colourless transparent crystals, with 6 Aq. When treated with hydrochloric, or any other acid, the sulphide of barium is decomposed, and the corresponding salt of baryta is formed, whilst sulphuretted hydrogen escapes; thus $BaS + HCl = BaCl + HS$.

(526) Chloride of Barium ($BaCl + 2\ Aq = 104 + 18$); *Sp. Gr., anhydrous*, 3·750, *cryst.*, 2·664.—This salt is obtained by dissolving the sulphide of barium or the carbonate of baryta in hydrochloric acid. On the large scale it may be procured by fusing together 1 part of crude chloride of calcium (the residue of the preparation of carbonate of ammonia), with 2 parts of powdered native sulphate of baryta; chloride of barium and sulphate of lime are formed; the chloride is washed out rapidly with hot water, and purified by crystallization. Chloride of barium crystallizes in flat four-sided tables, containing 2 Aq., which may be expelled by heat: water dissolves nearly half its weight at 60°, and three fourths at 212°: the presence of hydrochloric or of nitric acid greatly diminishes its solubility. A solution of this salt is the usual test for ascertaining the presence of sulphuric acid in solutions, which it indicates by the formation of a white precipitate insoluble in nitric acid. If anhydrous baryta be introduced into a jar of hydrochloric acid gas it becomes incandescent; chloride of barium is formed, and water is condensed on the sides of the vessel.

Silicofluoride of Barium ($BaF,SiF_2 = 140$) is procured by adding silicofluoric acid to a salt of baryta; it is quickly deposited in microscopic crystals, which are insoluble in an excess of the acid. The salt is anhydrous. It is decomposed by ignition, which converts it into fluoride of barium. The silicofluoride of strontium is soluble, and hence silicofluoric acid may be employed to distinguish baryta from strontia.

(527) Sulphate of Baryta ($BaO,SO_3 = 116·5$; *Sp. Gr.* 4·59) is the principal native mineral of baryta. It occurs in the mountain limestone in large veins, and is found accompanying the ores of lead and other metals. It is met with both massive, and crystallized in modifications of the right rhombic prism. The name 'baryta'

is derived from βαρὺς, 'heavy,' in allusion to the high specific gravity of this compound, which is about 4·6. It is insoluble in water, and in all the acids except boiling concentrated sulphuric acid: as the solution in this acid cools, crystals of the sulphate are deposited. De Senarmont has found that when the recently precipitated sulphate is heated to 472°, in a sealed tube for 60 hours, with diluted sulphuric acid, or with a solution of bicarbonate of soda, microscopic crystals of the same form as those of the native sulphate of baryta are deposited upon the sides of the tube. At a bright red heat the sulphate fuses into a white enamel: and by boiling the powdered sulphate of baryta with the carbonate either of potash or of soda, or, more rapidly by fusing it with either of these salts, the artificial sulphate is partially converted into the carbonate. It may be easily formed by precipitating a salt of baryta with any soluble sulphate, when it falls as a heavy, white powder. If nitric acid, or any nitrate be present in the solution, the precipitate carries down with it a portion of the nitrate, and this can only be removed by long washing with boiling water. Sulphate of baryta is used as a *permanent white* by artists in water colours. It is also employed for adulterating white lead; when ground with oil, however, it becomes partially transparent, and impairs the opacity of the lead pigment.

NITRATE OF BARYTA ($BaO,NO_5=130{\cdot}5$; *Sp. Gr.* 3·284) crystallizes in anhydrous octohedra, when a solution of the carbonate of baryta in nitric acid is evaporated. It is insoluble in alcohol, and requires eight or ten times its weight of cold water, and 3 of boiling water, for solution. Nitric acid precipitates it in crystals from its solution, unless very dilute: when heated, it first decrepitates strongly, and afterwards fuses; on ignition, the whole of the acid is expelled, with an appearance of ebullition owing to the escape of oxygen and nitrogen, whilst pure baryta remains.

(528) CARBONATE OF BARYTA ($BaO,CO_2=98{\cdot}5$; *Sp. Gr.* 4·4) forms the mineral called *witherite*: it occurs, both massive and crystallized, usually in six-sided prisms terminated by six-sided pyramids. It is abundant in the lead veins in the north of England, and is also found in Styria and in Siberia. 100 parts of the carbonate contain 22·31 of carbonic acid, and 77·69 of baryta. It is easily prepared artificially by precipitating a salt of baryta by the carbonate of one of the alkalies; it then forms a white powder, which is very sparingly soluble in pure water, and is insoluble in water charged with saline matter: an aqueous solution of carbonic acid dissolves it rather freely. If suspended in a solution of sulphate of potash, or of sulphate of soda, in the cold, and fre-

quently agitated, freshly precipitated carbonate of baryta is converted into sulphate; but if sulphate of baryta be boiled with a carbonate of one of the alkalies, carbonate of baryta and sulphate of the alkali are produced. Ignition of the carbonate does not expel the carbonic acid, but if it be mixed with charcoal and intensely ignited, it is partially decomposed; pure baryta is obtained, and may be dissolved out with water. If mixed with an equal weight of carbonate of lime, carbonate of baryta is decomposed without much difficulty when ignited in a current of steam: the hydrate of baryta may be dissolved out of the mixture by water.

Carbonate of baryta is now manufactured to some extent as a substitute for a portion of the alkali in the making of plate and flint glass. The silicate of baryta fuses and becomes incorporated with the other silicates. This carbonate is prepared from the sulphate, which is reduced to the form of sulphide by ignition with carbonaceous matter: the sulphide is then dissolved in water, and decomposed by a current of carbonic acid: the carbonate is thus precipitated as a fine white powder (Richardson and Ronalds's translation of Knapp's *Technological Chemistry*, vol. ii. p. 450).

(529) Characters of the Salts of Barium.—The salts of barium are colourless. The carbonate and all the soluble salts act as powerful poisons, and have an acrid, disagreeable taste. The best antidote when they have been taken internally, is the sulphate of soda or of magnesia.

Salts of barium when in solution are easily recognised by giving with *sulphuric acid* a white precipitate of sulphate of baryta, which is insoluble in the acids. Barium is, for the purposes of analysis, usually estimated in the form of sulphate; 100 parts contain 65·66 of baryta, and 34·34 of sulphuric acid. The presence of the citrate, either of soda or ammonia, prevents the precipitation of sulphate of baryta in neutral and alkaline solutions; but these salts do not redissolve the sulphate of baryta after it has once been deposited. On acidulating the solution containing the citrates with hydrochloric acid, the sulphate of baryta is precipitated in the usual manner (Spiller).

With *carbonate of potash* or *of soda* a white precipitate of carbonate of baryta is produced in solutions which contain barium. *Hydrosulphate of ammonia* gives no precipitate in such solutions. *Phosphate of soda* gives a white precipitate, which is soluble in diluted nitric or hydrochloric acid. Salts of barium, when mingled with alcohol, tinge its flame of a yellow colour. They are distinguished from the salts of strontium by forming an insoluble silicofluoride of barium when mixed with *silicofluoric acid*, and by

yielding no immediate precipitate with *oxalic acid*, but the mixture on standing deposits tufts of acicular crystals of oxalate of baryta.

§ II. STRONTIUM ($Sr=43\cdot8$); *Sp. Gr.* 2·54.

(530) STRONTIUM is an element much less abundantly diffused than barium, which it closely resembles in properties. It is found both as carbonate and as sulphate, and is procured in the metallic state in the same way as barium, to which it bears a relation similar to that existing between potassium and sodium. Strontium is a malleable metal of a pale yellow colour. When heated in the air, it burns with a crimson flame, emitting sparks. Water is decomposed by it with evolution of hydrogen: diluted nitric acid dissolves it, but the concentrated acid is almost without action even when boiled upon it.

STRONTIA ($SrO=52$: *Sp. Gr.* 4·611) may be obtained from its nitrate by ignition. When mixed with water it slakes, and forms a crystalline hydrate ($SrO,HO+8\,Aq$; Bloxam); these crystals require 50 times their weight of cold and 2 of boiling water for solution; 8 equivalents of water are expelled by heat, the remaining equivalent being fixed at all temperatures; at a full red heat the latter hydrate fuses, furnishing a mass of sp. gr. 3·625: both the hydrate and its solution absorb carbonic acid rapidly from the air. No peroxide of strontium can be formed.

CHLORIDE OF STRONTIUM ($SrCl+6Aq=79\cdot3+54$; *Sp. Gr. anhydrous*, 2·96, *cryst.*, 1·603) crystallizes in slightly deliquescent needles, which require less than their weight of cold water for solution; alcohol dissolves it, and the solution burns with a crimson flame. Chloride of strontium is rendered anhydrous by a moderate heat; if heated strongly it fuses.

Silicofluoride of Strontium ($SrF,SiF_2=115$) is prepared by adding silicofluoric acid to a salt of strontia; it is tolerably soluble in water, thus furnishing a character which distinguishes the compounds of strontium from those of barium.

SULPHATE OF STRONTIA ($SrO,SO_3=92$; *Sp. Gr.* 3·9) is found crystallized in rhombic prisms isomorphous with those of sulphate of baryta; it is, however, easily distinguished from it by its lower density. Many specimens of this mineral have a delicate blue tint, whence it derives its mineralogical name of *celestine*: it often contains crystals of native sulphur. Sulphate of strontia is very sparingly soluble in water, but is taken up by boiling sulphuric acid, and is soluble to some extent in a solution of chloride of

sodium. It may be formed by mixing a solution of any sulphate with a solution of a salt of strontium.

NITRATE OF STRONTIA ($SrO,NO_5=106$; *Sp. Gr.* 2·704) crystallizes from hot concentrated solutions in anhydrous octohedra, which are soluble in 5 parts of cold water and half their weight of boiling water; by crystallizing it at a low temperature it may be obtained in efflorescent crystals with 5 Aq. If strongly heated, it decrepitates, and then loses acid and leaves pure strontia. It is used by the makers of fireworks to give a splendid crimson colour to their flames, and is prepared for them by reducing the native sulphate to sulphide by heating it with charcoal, dissolving the sulphide in water, and decomposing it with diluted nitric acid. It crystallizes best from an acid solution. A mixture of 40 parts of nitrate of strontia with from 5 to 10 of chlorate of potash, 13 of sulphur, and 4 of sulphide of antimony, deflagrates with a magnificent red colour; the mixture is dangerous both to prepare and to preserve, having more than once been the occasion of frightful accidents to the manufacturers from its becoming ignited spontaneously. Nitrate of strontia is insoluble in alcohol.

CARBONATE OF STRONTIA ($SrO,CO_2=74$; *Sp. Gr.* 3·65), the *strontianite* of mineralogists, occurs both massive and crystallized, near Strontian in Argyleshire, and hence the name 'strontia' given to the earth which it contains. Mere ignition is insufficient to expel carbonic acid from this salt. It is scarcely soluble in water, but is dissolved by a solution of carbonic acid. The process of preparing it consists in precipitating a salt of strontia by the carbonate of one of the alkalies.

(531) CHARACTERS OF THE SALTS OF STRONTIUM.—The salts of strontium with colourless acids are all colourless: they have a bitter acrid taste, but are not poisonous. They are distinguished *before the blowpipe*, by the red colour which they communicate to the flame. Reagents produce upon them the same effects as upon salts of barium, excepting that neither *silicofluoric acid* nor the *hyposulphite of soda* yields any precipitate in the solutions of the salts of strontium. *Oxalic acid* gives an immediate turbidity in them. The compounds of strontium are distinguished from those of calcium by the gradual formation of a white precipitate on agitation after the addition of a solution of *sulphate of lime*. The sulphate of strontia is used for determining the amount of this earth in analysis: it contains in 100 parts 56·52 of strontia.

§ III. Calcium (Ca=20). *Sp. Gr.* 1·578.

(532) Calcium forms one of the most abundant and important constituents of the crust of the globe. It is the metallic basis of lime, and derives its name from *calx,* lime. Calcium occurs in nature in combination with fluorine, forming the different varieties of fluor-spar; it is still more abundant in the various forms of carbonate of lime, in which it is united with oxygen and carbonic acid; and it is also met with in large quantities as gypsum, which is a hydrated sulphate of lime.

Calcium was obtained by Matthiessen (*Q. J. Chem. Soc.*, viii. 28) by the electrolytic decomposition of a mixture consisting of 2 equivalents of chloride of calcium and 1 equivalent of chloride of strontium. The mass may be fused in a Hessian crucible, in the centre of which is placed a porous tube filled with the same mixture, and into this an iron wire passed through the stem of a tobacco pipe is inserted: this wire is connected with the platinode of the battery, the zincode of which consists of a plate of sheet iron bent into a cylindrical form, and immersed in the melted mass exterior to the porous tube: the calcium is reduced, and preserved from oxidation by so regulating the heat that a film of solidified salt shall form upon the surface of the mixture in the porous cell. Lies Bodart obtains it still more easily by fusing iodide of calcium with an equivalent quantity of sodium.

Calcium is a light yellowish metal, of the colour of gold alloyed with silver; in hardness it is intermediate between lead and gold; it is very malleable, and can readily be hammered into leaves thinner than writing paper. It melts at a red heat. At ordinary temperatures it tarnishes within a day or two, even in dry air, and in the presence of moisture it is slowly oxidized. When heated to redness on platinum foil, it burns with a brilliant scintillating white light. It readily amalgamates with mercury: when heated in chlorine, or in the vapour of bromine, iodine, or sulphur, the combustion is accompanied by an extremely vivid light. Water is rapidly decomposed by calcium, lime being formed and hydrogen evolved. Concentrated nitric acid does not attack the metal until heated to the boiling point, though it is rapidly dissolved by the diluted acid. Matthiessen found that the chloride of calcium is not decomposed by heating it with potassium or sodium; and he concludes that the properties formerly assigned to calcium were really due to a mixture of potassium with aluminum and silicon.

(533) Lime ($CaO=28$); *Sp. Gr.* 3·18.—Calcium forms only

one oxide—viz., lime, which has been known from time immemorial. It is obtained in a state of purity by heating pure carbonate of lime (541) to full redness; this carbonate occurs very nearly pure either in black or in Carrara marble, which if burnt for an hour or two in an open fire—or, better still, in a crucible with a hole at the bottom—yields lime very nearly free from foreign matters. For commercial purposes, common limestone, which is an impure carbonate of lime, is burned in a kiln, the cavity of which is usually egg-shaped. Over the fire-grate an arch is formed with lumps of limestone, and the kiln is filled up with smaller fragments, the fire is then kindled below, and kept up continuously for three days and nights; the kiln is then allowed to cool, the lime is removed, and a fresh charge introduced. A better method is that known as the continuous process. The kiln in this case is in the form of an inverted truncated cone: it is charged with alternate layers of coal and limestone, and the fire is kindled. The lime, as it is burned, gradually sinks down, and is removed by openings at the base of the furnace, and a fresh supply of coal and limestone is supplied at the top of the kiln. The limestone should not be too dry; that which has been quarried recently answers best. In damp weather, too, the operation succeeds better than in a dry state of the atmosphere; indeed, the process is facilitated by injecting steam into the kiln, although in practice the advantage which is gained does not compensate for the increased expense and trouble. In the presence of aqueous vapour an interchange between the steam and the carbonic acid of the limestone appears to be effected, and hydrate of lime is formed; but the hydrate which is produced is quickly destroyed again.

Pure lime, or *quicklime*, is a white caustic powder which resists even the heat of the oxyhydrogen flame, and emits an intense white light when thus ignited, as is commonly seen in its application to the Drummond light. The extreme infusibility of lime has led Deville to employ it as a material for lining crucibles which are to be exposed to very intense heat.

Hydrate of Lime, Slaked Lime ($CaO,HO=37$); *Sp. Gr.* 2·078. —When water is poured upon lime, it swells up and enters into combination with the water; if the proportion of water be not too great, a light dry powder is formed, attended with a powerful extrication of heat: so great is the heat thus developed that fires have several times been traced to this source. The hydrate which is formed is a definite compound of 1 atom of water with 1 of lime. Lime, when exposed to the air, slowly attracts both water

and carbonic acid; as a result of this action it falls to powder, and becomes what is termed *air slaked;* in this case a compound is gradually formed, which is by some chemists regarded as a combination of an atom of carbonate with one of hydrate of lime ($CaO,CO_2 + CaO,HO$).

Lime is soluble in about 700 parts of cold water; this solution is known as lime water; the earth, however, is less soluble in hot than in cold water, so that if lime water saturated in the cold be raised to the boiling point, half the lime is deposited. Lime is much more soluble in syrup than it is in water, the solution in this case also becomes turbid when heated, but clears again as it cools. Lime water is much employed as a test for the presence of carbonic acid, which instantly renders it turbid: it has a distinctly alkaline reaction, and an acrid taste: by evaporating it in vacuo, Gay Lussac obtained from it the protohydrate of lime crystallized in hexahedral plates. Hydrate of lime is decomposed by a red heat, and pure lime remains.

Milk of Lime is merely hydrate of lime diffused through water: in slaking lime for its preparation, and indeed, generally where small quantities of the hydrate are required in a fine state of subdivision, it is best to use boiling water in quantity nearly equal to twice the weight of the lime; the powder may afterwards be readily diffused through cold water.

(534) *Mortars and Cements.*—The great consumption of lime in the arts is for the purpose of making mortars and cements. Pure lime, when made into a paste with water, forms a somewhat plastic mass, which sets into a solid as it dries, but it gradually cracks and falls to pieces. It does not possess sufficient cohesion to be used alone as a mortar; to remedy this defect and to prevent the shrinkage of the mass, the addition of sand is found to be necessary. Ordinary mortar is prepared by mixing 1 part of lime into a thin paste with water, and adding 3 or 4 parts of sharp sand, of tolerable fineness: the materials are then thoroughly incorporated, and passed through a sieve to separate lumps of imperfectly burned lime: a suitable quantity of water is afterwards worked into it, and it is then applied in a thin layer to the surfaces of the stones and bricks which are to be united. The bricks or stones are moistened with water before applying the mortar, in order that they may not absorb the water from the mortar too rapidly. The completeness of the subsequent hardening of the mortar depends mainly upon the thorough intermixture of the lime and sand.

The theory of the hardening of mortar is obscure. The mortar gradually becomes dry upon its surface, and at the same time it

absorbs carbonic acid from the air; but this change is never complete, for the central portions, after a lapse of many ages, are still found to contain free lime in abundance: mortar taken by Dr. Malcolmson from the Great Pyramid was still found to contain a large proportion of hydrate of lime. A gradual combination also takes place between the lime and the silica of the sand: each grain of sand thus becomes superficially converted into a hydrated silicate of lime, forming a compound which by degrees acquires considerable hardness, and contributes greatly to the solidification of the mortar. All old mortar, when treated with an acid, yields a small proportion of gelatinous silica. A mixture of carbonate of lime with the lime appears to set harder than pure lime only; so that for many purposes lime which has been slaked by exposure to the air, and contains a considerable proportion of carbonate, is preferred to that slaked rapidly by water.

Limestones vary greatly in composition; being rocks of sedimentary origin, they are not pure chemical compounds, but consist of a mixture of various bodies, in which carbonate of lime is the prevailing ingredient. The different varieties of limestone are distinguished according to the nature of the most important of these admixtures. Thus a limestone is described as magnesian, argillaceous, ferruginous, sandy, or bituminous, according as it is characterized by the presence of carbonate of magnesia, clay, oxide of iron, sand, or bituminous matter. These different limestones, when burned, yield lime of very different characters, which are particularly manifested by the action of water upon them. The purer the lime, the more quickly does it combine with water when mixed with it. Such pure limes are technically termed *rich* or *fat* limes; when the amount of impurities present does not exceed 10 per cent. they slake rapidly, during which operation they swell up and greatly increase in bulk; they become extremely hot, and yield a soft, fine, dense paste: while those which contain much magnesia, silica, or alumina, slake slowly, emit but little heat, and are technically termed *poor*.

In slaking for mortar, a fine smooth paste is required: in order to secure this point, the slaking should be effected quickly, with about 3 parts of water to 1 part of lime; the mass, if composed of a fat lime, then swells to between 3 and 4 times its former bulk: if too little water be used, a crystalline granular hydrate is formed.

The temperature required for burning lime varies with the composition of the limestone. When a siliceous limestone is burnt, the silica combines with the lime if the temperature be too high

and be too suddenly raised, and a coating of silicate forms on the surface of the mass, which becomes partially vitrified. Such lime slakes very imperfectly, and is said to be *dead burnt*. If ordinary quicklime be mixed with a small quantity of sulphate of lime, or if it be re-burnt at a dull red heat in an atmosphere containing a small proportion of sulphurous acid, it acquires the property of setting slowly like stucco when mixed with cold water, but if boiling water be used it slakes like common lime. Lime so prepared is known as *Scott's cement*.

(535) *Hydraulic Mortars.*—Ordinary mortar, when placed in water, becomes gradually softened and disintegrated, whilst the lime is dissolved away. It cannot therefore be used for subaqueous constructions. Some poor limes, however, which contain from 15 to 35 per cent. of finely divided silica or clay, furnish a mortar which possesses the valuable property of hardening under water, forming what are termed *hydraulic limes*. These limes may be artificially imitated by mixing with the lime a due proportion of clay not too strongly burnt. At Puzzuoli, near Naples, a porous volcanic material, which has received the name of *puzzuolana*, is found. This substance, when powdered and mixed with ordinary lime, confers upon it the property of yielding an excellent hydraulic mortar, which was employed by the Romans in many of their buildings, in which it is still in perfect preservation, having resisted the ravages of time more perfectly than the bricks which it was used to cement. It is found that a puzzuolana which is easily attacked by sulphuric acid is more effective than one which resists the action of the acid. The comparative value of a puzzuolana may also be roughly and rapidly estimated by taking a given measure of lime water and agitating it with successive small quantities of finely powdered puzzuolana until the alkaline reaction disappears; the puzzuolana combines with the lime, and abstracts it from the water. The smaller the quantity of the powder required, the more active are its hydraulic powers. Puzzuolana consists chiefly of silicates of alumina, lime, and soda.

Many other substances, when added to lime, confer upon it hydraulic properties to a greater or less extent. Gelatinous silica shows it slightly, and a mixture of hydrate of silica with freshly precipitated alumina or magnesia shows it in a remarkable degree. Sand, oxide of iron, and oxide of manganese, are destitute of this property. From a knowledge of these facts it is easy to convert ordinary lime into one possessed of hydraulic properties. Clay is a silicate of alumina; when it is heated with lime, decomposition occurs, the alumina is set free, and silicate of lime is formed.

The materials are in this way reduced to a condition suitable for use as a hydraulic cement; but great care is required in regulating the temperature. If it be allowed to rise too high, partial vitrification occurs, which impairs the tendency of the cement to combine with water; while, on the other hand, if the heat be insufficient, the alumina is not liberated from its combination with the silica. The immediate cause of the solidification of these hydraulic limes appears to be the formation of a hydrated compound of lime with the silica and alumina, which is very hard, and insoluble in water.

The manufacture of artificial hydraulic lime was first established upon sound principles by Vicat. He proceeds thus in its preparation:—Four parts of chalk are ground and levigated in water with 1 part of clay, so as to obtain a very intimate mixture of the materials, which are allowed to subside, moulded into blocks, dried, and calcined at a carefully regulated temperature. *Portland Cement* is a hydraulic mortar similar to the above. It is made from clay obtained from the valley of the Medway, and from chalk found in the same neighbourhood: it derives its name from the circumstance that in colour, when dry, it resembles Portland stone. It is prepared by thoroughly grinding the clay and chalk with water, allowing them to subside, then drying and burning the mixture until it undergoes slight vitrification; the mass is again ground, and when mixed with a proper proportion of water, it forms a cement which possesses great hardness and tenacity; it expands as it solidifies. If in preparing this cement the lime be first burned and then mixed with clay and reburned, it does not require more than a full red heat to produce a good cement.

Hydraulic limes do not slake with any considerable emission of heat when moistened; they absorb the water without increasing much in bulk, and form a paste of small plasticity. In order that hydraulic lime may harden properly, it must not be submerged till it begins to set; it should then be kept moist until it is quite hard, otherwise it always remains porous.

The rapidity with which these different kinds of hydraulic limes set, varies considerably with their composition. If the clay do not exceed 10 or 12 per cent. of the weight of the original limestone, the mortar requires several weeks to harden. If the clay amount to from 15 to 25 per cent. it sets in two or three days, and if from 25 to 35 per cent. of clay be present, the solidification occurs in a few hours. The substance to which the term *Roman cement* is now applied, is a lime of this latter description. Roman cement is extensively prepared from nodules of septaria which occur

in the valley of the Thames. It sets in a few hours after the mixture with water has been effected, and it soon rivals stone in hardness. According to Meyer, the composition of the nodules employed in the preparation of the cement is the following :—

Matter soluble in acid 76·0	Carbonate of lime	66·99
	„ magnesia	1·67
	„ iron	6·95
	Alumina	0·39
Insoluble in acid (Clay) 23·305	Silica	16·89
	Alumina	4·32
	Oxide of iron	1·72
	Lime	·005
	Magnesia	0·37

The cement obtained from the neighbourhood of Boulogne is almost identical in composition with the foregoing; and similar materials have been obtained in other countries, particularly in the beds of the Jurassic formation.

Concrete is a mixture of hydraulic mortar with small pebbles coarsely broken.

(536) *Other Uses of Lime.*—Lime is also largely employed as a manure, and it is particularly valuable upon very rich vegetable soils, such as those formed over peat bogs: its effects in these cases are partially due to the decomposition of the organic matter, which it renders soluble and capable of assimilation, while the lime itself is converted into carbonate. It has been found that limestone containing much carbonate of magnesia yields a lime unsuited to agricultural purposes: this has been attributed to the fact that magnesia absorbs carbonic acid much more slowly than lime, and remains caustic for a longer period, in which state it appears to be injurious to the tender shoots of the young plants.

The strong affinity of lime for carbonic acid renders it a valuable material for separating this acid from the carbonates of potash and soda, when these alkalies are required in a caustic form. Its attraction for water furnishes a means of removing this liquid from many substances, such as alcohol, which retain it with considerable force; the finely powdered lime is mixed with the alcohol, and the mixture after being allowed to stand for a few days, with occasional agitation, is subjected to distillation: the anhydrous alcohol passes over, leaving the water combined with the lime. Lime is employed also as a direct chemical agent in the purification of coal-gas, and as a means of loosening the epidermis, and facilitating the removal of the hair from hides, as a preliminary to the process of tanning.

Binoxide of hydrogen forms an insoluble compound with lime,

which is precipitated in crystalline scales when the binoxide is poured into lime water: it is very unstable, and undergoes spontaneous decomposition at the temperature of the air. This substance has been described as *binoxide of calcium*.

(537) SULPHIDES OF CALCIUM.—Calcium forms several compounds with sulphur, all of which are soluble. An insoluble oxysulphide is produced during the preparation of black ash (491), said to consist of 3 CaO,CaS, but its exact composition is doubtful.

The *protosulphide of calcium* ($CaS=36$) is procured by decomposing a mixture of sulphate of lime and charcoal by heat, as directed for sulphide of barium. It is very sparingly soluble in water, and is phosphorescent when newly prepared. This property was first observed by Canton, in an impure sulphide of calcium, which he obtained by calcining oyster shells in an open fire for half an hour, then selecting the whitest and largest portions, and packing them with one third of their weight of flowers of sulphur in a crucible with a luted cover; this was heated strongly for an hour: when cold, the crucible was broken, and the whitest pieces were placed in well-closed bottles.

By boiling slaked lime with excess of sulphur, a *pentasulphide of calcium* is obtained, and hyposulphite of lime is formed at the same time: $3\,CaO+12\,S=2\,CaS_5+CaO,S_2O_2$.

(538) PHOSPHIDE OF CALCIUM ($Ca_2P\,?=71$).—This compound presents some interest, from its affording the most convenient source of the phosphides of hydrogen (376). It is prepared by distilling phosphorus over lime heated to low redness: a mixture of phosphide of calcium and phosphate of lime is the result, $7\,P+14\,CaO=2(2\,CaO,PO_5)+5\,Ca_2P$ (P. Thénard). The most convenient method of conducting the operation is shown in fig. 318. In the lower part of a narrow deep crucible, A, a hole is drilled for the reception of the neck of a flask, B, which is luted into the aperture; a quantity of dry phosphorus is placed in the flask, and the crucible is filled with quicklime, broken into fragments of about the size of a hazel nut; a lid is then luted upon the top of the crucible. Time having been given for the luting to become dry, the upper part of the crucible is raised to a red heat as quickly as possible, by surrounding it with ignited charcoal, the lower part of the furnace having been filled with cold charcoal, to prevent the heat from reaching the phosphorus too rapidly; the phosphorus becomes

FIG. 318.

gradually volatilized as the heat reaches it. If the heat be too high, the phosphorus distils over without combining with the calcium.

Phosphide of calcium when procured in this manner forms an anhydrous mass of a dull red colour, hard enough to strike fire with steel; it experiences no change in dry air or in oxygen at the ordinary temperature. At a high temperature it becomes partially decomposed by oxygen, chlorine, or hydrochloric acid; in a moist atmosphere it slakes, emits phosphuretted hydrogen, and crumbles to a brown powder. This powder, when thrown into water, or heated to 212°, evolves phosphuretted hydrogen, which is not self-lighting, and is mixed with free hydrogen.

Phosphide of calcium, in its unslaked form, is decomposed when thrown into water; phosphuretted hydrogen gas is evolved, and takes fire with the phenomenon already described (377): diluted acids produce its decomposition still more rapidly.

(539) CHLORIDE OF CALCIUM ($CaCl + 6\,Aq = 55\cdot5 + 54$); *Sp. Gr. fused*, 2·485, *cryst.* 1·680.—This salt is obtained as a secondary product in the manufacture of carbonate from muriate of ammonia, but it may be prepared by dissolving chalk in hydrochloric acid, evaporating to dryness, and fusing the residue at a red heat. Under these circumstances, a small portion of the chlorine is displaced by the oxygen of the air, so that the mass has an alkaline reaction, owing to the presence of lime. By evaporation of its solution it may be obtained in striated prismatic four-sided crystals with 6 Aq, which fuse at 84°. In this form it produces great depression of temperature when dissolved in water, and if mixed with snow it furnishes a powerful freezing mixture. If the hydrated salt be exposed to a prolonged heat of 300° it forms a porous mass which still retains 2 Aq; in this state it is well adapted for the desiccation of gases. Chloride of calcium is extremely deliquescent; a saturated solution of the salt boils at 355°, and is sometimes employed where a steady temperature, not exceeding this point, is required. It is soluble in alcohol, and may be obtained from its alcoholic solution crystallized in rectangular plates, containing 2 equivalents of alcohol. Chloride of calcium absorbs ammonia rapidly, and forms a compound with 4 equivalents of the gas. A solution of the chloride, if boiled with quicklime and filtered while hot, deposits long, flat, thin crystals of a hydrated oxychloride, consisting of ($CaCl, 3\,CaO + 15\,Aq$), which is decomposed both by water and by alcohol.

(539 *a*) FLUORIDE OF CALCIUM ($CaF = 39$; *Sp. Gr.* 3·14) is an abundant mineral, well known as *fluor-spar*, which occurs either massive, or crystallized in forms allied to the cube. It is found

accompanying the lead veins in Cumberland, Derbyshire, and Cornwall, and is met with in a variety of other localities, of various colours, most frequently blue, green, or white. Fluor-spar is the principal source from which the compounds of fluorine are obtained. Fluoride of calcium, in minute quantity, is found in sea water (Dr. G. Wilson), and in many springs: it is a never-failing companion of phosphate of lime in the bones and teeth of animals, and indeed is always found to accompany phosphate of lime in the mineral kingdom also, in small but variable quantities. Most varieties of fluor-spar, when gently heated, become phosphorescent, emitting a pale green or violet light; if heated more strongly, the crystals decrepitate, and each fragment becomes enveloped for a few seconds in a beautiful halo of light. It loses this property after having been once heated; a phosphorescent fluor, dissolved in hydrochloric acid and precipitated by ammonia, retains its power of emitting light when heated, but if it had been previously heated sufficiently to destroy the phosphorescence, this property is not restored by solution and reprecipitation.

Powdered fluoride of calcium absorbs sulphuric acid if mixed with it at a low temperature, and forms a transparent, viscous mass, from which fumes of hydrofluoric acid are evolved by heating it to 100° F. Fluor-spar undergoes no change when heated with sulphuric anhydride, but with boracic anhydride it yields borate of lime and borofluoric acid. Hydrochloric acid dissolves it in small quantity. If heated in a current of chlorine, a gas which corrodes glass is expelled. It is not known whether this is fluorine or chloride of fluorine. When fluor-spar is fused with the alkalies it undergoes no change: with the carbonates of the alkalies, fluoride of the alkaline metal and carbonate of lime are formed. If heated with sulphate of lime, it fuses and forms a glass which is transparent when hot, but enamel-white when cold. In proper proportions it often forms a valuable flux in smelting the ores of various metals, and hence the name *fluor* is derived, though it requires rather an elevated temperature to fuse it when heated without any admixture.

(540) SULPHATE OF LIME ($CaO,SO_3=68$): *Sp. Gr.* 2·95; *crystallized as gypsum* ($CaO,SO_3+2\ HO=86$); *Sp. Gr.* 2·30.—This compound occurs free from water in the mineral *anhydrite*, crystallized in rectangular prisms, which are found in the salt rocks of the Tyrol, and in Upper Austria; but it is much more abundant as a hydrate with 2 Aq: it is then met with either in transparent flattened prisms, known as *selenite*, or still more frequently in a fibrous, granular, compact, or earthy form, constituting the dif-

ferent varieties of *gypsum* and *alabaster*. Sulphate of lime is a very common impurity in spring water. Such waters are termed *selenitic;* they deposit upon the interior of boilers in which they are used, a strongly adherent fur or crust, the composition of which is $2\ (CaO,SO_3)+Aq$; the sulphate being rather less soluble in water at 212° than at ordinary temperatures.

Sulphate of lime is produced whenever a strong solution of a salt of lime is precipitated by any sulphate, in which case it falls as a white voluminous sparingly soluble hydrate, which requires about 400 parts of water for its solution. It is insoluble in alcohol, but is dissolved to some extent by diluted nitric and hydrochloric acids. When heated it loses its water, and if the temperature be raised to bright redness, the anhydrous mass fuses, and may be obtained in crystals the same in form as those of anhydrite. 100 parts of the anhydrous salt contain 58·82 of sulphuric acid, and 41·18 of lime. Gypsum contains 20·93 per cent. of water.

Gypsum constitutes a manure of considerable utility when judiciously employed; but the most remarkable property of sulphate of lime, and that for which it is chiefly valued, is the power which the hydrated variety possesses, after it has been deprived of water by a heat not exceeding 500°, of again combining with water, and binding or setting into a hard mass. If the dry powder be made into a thin paste with water, the mixture becomes solid in a few minutes, expands considerably at the moment of solidification, and experiences a considerable rise of temperature, which in large masses may amount to 40° or 50°: a combination of 2 atoms of water with 1 atom of sulphate of lime occurs, and eventually it becomes as hard as the original gypsum. Gypsum which has been dried at a temperature of from 400° to 500° F. is converted into a white friable mass, which when ground to a fine powder is known in the arts under the name of *plaster of Paris,* from the circumstance of the mineral being extensively found in the environs of the French metropolis. It is however particularly worthy of observation, that if the sulphate be heated to redness, it becomes very much denser, assumes a crystalline structure, and loses the power of setting or solidifying when mixed with water, each atom of the salt recombining with the 2 atoms of water it had lost.

Plaster of Paris is manufactured in large quantities for architectural purposes: it is also extensively used in modelling, and in taking accurate copies of objects of every description. Suppose, for instance, it were desired to copy a medal: a raised rim of pasteboard is attached to the medal, which is anointed with a little oil, to prevent the plaster from adhering to its surface. The dried

plaster is then mixed with water till it is of the consistence of thin cream, and is immediately applied carefully with a hair pencil to every part of the surface, so as to exclude air; after which a thicker cream is poured into the mould: in a few minutes the mass becomes solid, and the cast may be removed from the medal.

The addition of 1 or 2 per cent. of many salts—particularly of alum, of sulphate of potash, or of borax—confers upon gypsum some properties of considerable practical importance. Gypsum which has been thus treated will endure a dull red heat without losing its power of setting when mixed with water. It becomes much denser than ordinary plaster, and, when mixed with water, sets in the course of a few hours, and forms a hard material which takes a high polish. Keene's, Martin's, and Keating's cement are the names under which plaster so treated is known. *Stucco* consists of coloured plaster, mixed with a solution of size. The different colours exhibited by stucco are obtained by the admixture of oxides of iron and other metals. By friction its surface is susceptible of a high polish.

Polyhallite is the mineralogical name for double sulphate of potash and lime ($KO,CaO, 2SO_3+Aq$), which is sometimes found native, and has been formed occasionally during the manufacture of tartaric acid. It is decomposed by water.

Sulphate of lime also forms a double salt with sulphate of soda, which occurs native under the name of *glauberite* ($NaO,CaO, 2SO_3$); it is anhydrous, and nearly insoluble in water.

NITRATE OF LIME ($CaO,NO_5+4Aq=82+36$; *Sp. Gr. anhydrous*, 2·24, *cryst.* 1·780) is a deliquescent salt, which crystallizes in long prisms; when anhydrous, it emits light if gently heated. It is soluble in alcohol.

(541) CARBONATE OF LIME ($CaO,CO_2=50$): *Sp. Gr. of Iceland spar*, 2·72; *of Aragonite*, 2·97.—This substance is one of the most abundant components of rocks and minerals. In the amorphous condition, it forms the different varieties of limestone, oolite, chalk, and calcareous marl; it is the principal constituent of corals, of the shells of fishes, and of the eggshells of birds; it also enters in greater or less quantity into the bones of animals. In minute granular crystals it forms the different kinds of marble, and it is found in a greater variety of regular crystalline forms than any other known compound. Its primary form is a rhombohedron, as is seen in Iceland spar, but it also occurs in the incompatible form of aragonite, in six-sided prisms, and is consequently dimorphous. Aragonite is isomorphous with carbonate of strontia, and its crystals not unfrequently contain small quantities of this mine-

ral, the occurrence of which it is supposed may assist in determining the assumption of the prismatic form by the carbonate of lime. When aragonite is heated it falls to powder, and the grains are stated to assume the form of minute rhombs. Carbonate of lime is produced whenever a salt of lime is precipitated by the addition of an alkaline carbonate, and if the solutions be mixed at the boiling point, the carbonate falls in microscopic crystals, having the form of aragonite. 100 parts of carbonate of lime contain 44 of carbonic acid and 56 of lime.

It is sometimes necessary to obtain a perfectly pure carbonate of lime; for this purpose a solution of nitrate of lime may be mixed with an excess of lime water, which precipitates magnesia, alumina, oxide of iron, and other metallic oxides; the filtered solution is decomposed by the addition of a mixture of ammonia and sesquicarbonate of ammonia; the precipitate is washed thoroughly, then dried, and heated to low redness.

Carbonate of lime is decomposed by a red heat, if the acid can freely escape; but in closed vessels it fuses without undergoing decomposition, and on cooling becomes converted into a granular crystalline mass, like marble.

A combination of the carbonates of lime and soda, insoluble in water, was found at Merida, in South America, and called *Gay-Lussite* ($CaO,NaO, 2\ CO_2, +6\ Aq$). *Barytocalcite* ($CaO,BaO, 2\ CO_2$) is a native double carbonate of lime and baryta, which crystallizes in oblique prisms.

(542) *Calcareous Waters.*—Carbonate of lime is soluble in pure water to the extent of rather more than 2 grains in 1 gallon, but it is freely taken up by water charged with carbonic acid, and is deposited again in anhydrous crystals as the gas escapes. In this way enormous masses of crystallized carbonate of lime are formed. In the limestone hills of Derbyshire, and in various other localities, caverns occur in which this phenomenon is perpetually exhibited; water charged with carbonic acid and carbonate of lime makes its way through the roof of the cavern, where, as the carbonic acid gradually escapes, the carbonate of lime is deposited in dependent masses, like icicles, termed *stalactites;* whilst the water falling on the floor of the cavern before it has parted with all its excess of carbonic acid and dissolved limestone, deposits a fresh portion of the crystalline matter; and thus a new growth, or *stalagmite*, gradually rises up to meet the stalactite which depends from the roof: in this way a natural pillar of crystallized carbonate of lime is formed.

It is in a similar manner that the calcareous deposits from the lakes of volcanic districts are produced. These deposits, when

porous, have received the name of *tufa;* when more compact, they are termed *travertine.* Travertine is formed abundantly in many of the Italian lakes; it was highly valued for architectural purposes by the Romans, as it is a material easily wrought, and possesses great durability and beauty.

Many spring waters contain carbonate of lime held in solution by carbonic acid : when the water is boiled this acid is expelled, and the carbonate is deposited, forming a lining more or less coherent upon the sides of the vessel. In steam boilers this becomes a serious evil: it is effectually prevented by the addition of a small quantity of sal ammoniac to the water; carbonate of ammonia is formed, and volatilized, while chloride of calcium remains dissolved.

Dr. T. Clark has introduced a plan for softening such calcareous waters, by removing the carbonic acid from them, and causing the precipitation of the carbonate of lime by thus depriving it of its solvent. This method consists essentially in the addition of milk of lime to such waters, until the water gives a very faint brown tinge on testing it with a solution of nitrate of silver; this reaction indicates that a slight excess of lime has been added, which occasions a precipitate of brown hydrated oxide of silver. In this operation the lime combines with the excess of carbonic acid in the water; the carbonate of lime thus formed, being insoluble, is precipitated along with the portion of carbonate of lime previously held in solution by the carbonic acid. After the lapse of twenty-four hours the water becomes perfectly bright and clear. If colouring or organic matters be present in the water, a considerable portion of both goes down with the chalk. In applying this process upon a large scale, it is found advantageous to add a slight excess of lime in the first instance, and afterwards to destroy this excess by a fresh addition of unlimed water. The carbonate of lime is then separated in granular crystals, which speedily subside. These crystals are formed much more slowly if the lime be not first in slight excess.*

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* Dr. Clark has introduced a method of testing the hardness of waters by the application of the *Soap-test*, which has been extensively used. The operation may be conducted in the following manner:—

A solution of soap in proof spirit (containing about 120 grains of curd soap to the gallon) is first prepared. In order to graduate this solution, 16 grains of Iceland spar, or Carrara marble, are dissolved in a flask in pure hydrochloric acid, evaporated to dryness in the flask, redissolved in water, and a second time evaporated to dryness. On again dissolving it in water, a perfectly neutral solution of chloride of calcium is obtained; this solution is then diluted with distilled water until it measures 1 gallon. It will now represent a water of 16° of hardness; that is to say, it will correspond in hardness to a water containing 16 grains of carbonate of lime per gallon, each degree of hardness upon Clark's scale representing an amount of any salt of

(543) *Building Materials.*—Carbonate of lime forms the basis of some of the materials most highly prized for building purposes, besides furnishing the costly varieties of marble used for interiors. The oolites, such as those from the Isle of Portland and the neighbourhood of Bath, resist the weather admirably; they admit of being readily fitted and cut, and yet possess considerable hardness. Many shelly limestones are also well adapted for these purposes.

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lime corresponding to 1 grain of chalk per gallon in the water. 1000 water-grain measures of this solution are next transferred by a pipette, graduated to deliver exactly this quantity, into a bottle which will hold 5 ounces, and accurately fitted with a glass stopper. The soap solution is then added to the water from a burette, each division of which corresponds to 10 water-grains. After each addition of the soap-test, the stopper is replaced in the bottle, and the bottle is briskly shaken for a minute, after which it is laid upon its side; fresh portions of the soap being added in small quantities until a fine lather in uniform small bubbles remains unbroken over the surface for three minutes. The number of measures of the soap-test employed is noted, and the strength of the solution is increased or diminished by the addition of soap or of spirit, as may be necessary, until exactly 32 measures are required for 1000 water grains of the standard solution of 16° of hardness. After the solution has been made up to this strength, the experiment is repeated, in order to ascertain that the adjustment is correct.

In applying the test, 1000 measured grains of the water to be examined are introduced into the stoppered bottle, and the operation is proceeded with as above directed, reading off the number of test-measures required, in order to produce a permanent lather. The degree of hardness of the water is then obtained by simple inspection of the subjoined table. The results are, however, apt to be inaccurate, if large quantities of magnesian salts are present. Sometimes the water exceeds 16° in hardness; in that case it should be diluted with an equal measure, or, if necessary, with twice, or even with thrice its bulk of distilled water. 1000 grain-measures of the diluted water are then to be tested as usual, and the number of divisions of the soap-test employed is to be read off, and the degree of hardness corresponding to it is noted from the table. This degree must be finally multiplied by 2, by 3, or by 4, according to the extent to which the water had been previously diluted.

Clark's Table of Hardness of Water.

Degree of hardness.	Measures of soap-test.	Diff. for the next 1° of hardness.
0 (Distilled water)	1·4	
		1·8
1	3·2	
		2·2
2	5·4	
		2·2
3	7·6	
		2·0
4	9·6	
		2·0
5	11·6	
		2·0
6	13·6	
		2·0
7	15·6	
		1·9
8	17·5	
		1·9
9	19·4	
		1·9
10	21·3	
		1·8
11	23·1	
		1·8
12	24·9	
		1·8
13	26·7	
		1·8
14	28·5	
		1·8
15	30·3	
		1·7
16	32·0	

Where elaborate carving is required, a well-crystallized magnesian limestone (or double carbonate of lime and magnesia), such as that employed in the new Houses of Parliament, is preferred; it is very close and compact, sufficiently soft to be easily sculptured, but retains a sharp outline. Many fine-grained, porous, calcareous and magnesian stones have the inconvenience of splitting into flakes after a few years' exposure; this generally occurs from the absorption of water, and its expansion when the moisture thus absorbed becomes frozen during winter. A simple and ingenious mode of ascertaining whether a building stone is liable to this defect was invented by Brard:—it consists in taking a smoothly cut block of the stone, one or two inches in the side, and placing it in a cold saturated solution of sulphate of soda. The temperature of the solution is gradually raised to the boiling point, it is allowed to boil for half an hour, and then the stone is left to cool in the liquid. When cold, it is suspended over a dish, and once a day for a week or a fortnight, plunged for a few moments into a cold saturated solution of the sulphate of soda, and is then again freely suspended in the air. The sulphate of soda crystallizes in the pores of the stone, and splits off fragments of it. A similar experiment is made upon an equal sized mass of stone which is known to be free from this defect. By the comparative weight of these fragments in the two cases the tendency of the stone to the defect in question may be estimated.

A stone which is placed in a building conformably to its position in the quarry, so that its seams shall lie horizontally, is much less liable to injury from the weather than where this point is neglected.

In the selection of a building-stone, regard must be had not merely to its durability, but also to the locality in which it is to be placed. A stone which, like a magnesian limestone, may endure unchanged for ages in the open country air, may yet in the atmosphere of a large city become rapidly disintegrated, owing to the action of the sulphuric acid produced by the immense quantities of coal which are burned. Decay from this cause is strikingly shown in the stone used in some parts of the new Houses of Parliament, and still more so in the new buildings in Lincoln's Inn.

A valuable report upon the composition and quality of various kinds of building stones was made to the British Government in 1839, upon the occasion of the rebuilding of the Houses of Parliament.

The other varieties of building stones are mostly siliceous. To this class belong all the sandstones, which consist chiefly of grains

of silica united by a cement more or less ferruginous. The durability of the stone depends mainly upon the character of this uniting material. Many igneous rocks, such as porphyry, basalt, and more especially granite, are also used for building purposes; but from their hardness, they are seldom wrought, except when, as in quays, bridges, or causeways, the constant wear is unusually great, and where softer though less expensive materials would soon be destroyed.

(544) Phosphates of Lime.—The most remarkable of the phosphates of lime is that known as the *bone phosphate* ($3\,CaO, PO_5$), from its forming the principal earthy constituent of the animal skeleton. It is easily procured by adding chloride of calcium, drop by drop, to a solution of phosphate of soda in excess, when it falls as a gelatinous precipitate with 2 Aq. It may also be obtained from calcined bones by digesting them in nitric acid, and precipitating the filtered solution by caustic ammonia. 100 parts of the anhydrous phosphate contain 45·8 of phosphoric acid and 54·2 of lime. This phosphate is insoluble in water, but is readily dissolved by acetic, and the stronger acids. It occurs native as a white amorphous mineral, known under the name of *phosphorite*. In the Norfolk crag considerable deposits of brown rounded pebbles occur, known under the erroneous name of *coprolites*; they contain a large proportion of phosphate of lime mixed with carbonate of lime and fluoride of calcium. In the greensand formation near Farnham, and in other localities, nodules chiefly composed of phosphate of lime are also found abundantly.

A tribasic phosphate of lime occurs naturally crystallized in hexagonal prisms, which, when colourless, are called *apatite*; when of a green colour it is termed *moroxite*; in these minerals the phosphate is associated with variable quantities of fluoride of calcium. If bone-ash be fused with about 4 times its weight of chloride of sodium, and allowed to cool very slowly, delicate crystals having the form of apatite are found lining the cavities contained in the mass (Forchhammer). When rhombic phosphate of soda is added drop by drop to an excess of chloride of calcium, a semi-crystalline precipitate falls, which, according to Berzelius, consists of ($2\,CaO, HO, PO_5 + 3\,Aq$).

Several other phosphates of lime may be formed, corresponding in composition to the various phosphates of soda. The soluble acid phosphate, or *superphosphate of lime* ($CaO, 2\,HO, PO_5$), is prepared by treating bone-earth with two thirds of its weight of oil of vitriol, as in the preliminary stage of the extraction of phosphorus. It is largely manufactured as a manure for turnips.

(544 *a*) A double *Borate of Lime and Soda, Boro-natro-calcite* [$NaO, 2\,BO_3 + 2\,(CaO, 2\,BO_3) + 18\,Aq$] is found at Iquique, in Peru, in the form of rounded nodules, composed of fine silky needles. It is but sparingly soluble in hot water, to which it communicates an alkaline reaction; but it is easily dissolved by diluted acids. This mineral has recently been imported into this country to some extent for the preparation of borax, which is easily obtained from it by dissolving the compound in hot diluted hydrochloric acid, and precipitating the lime as carbonate by the addition of carbonate of soda; the clear, supernatant liquid on evaporation yields crystals of borax, whilst chloride of sodium remains in solution.

(545) CHARACTERS OF THE SALTS OF CALCIUM.—The salts of calcium are colourless. They give no precipitate with *ammonia*, but yield a white precipitate of carbonate of lime, with the *carbonates of the alkalies*. Solution of *sulphate of lime* produces no precipitate; the calcium salts are thus distinguished from those of barium and strontium: they yield no precipitate with *hydrosulphate of ammonia*. *Oxalate of ammonia*, even in very dilute neutral or alkaline solutions of lime, throws down a white oxalate of lime, which is soluble in nitric and hydrochloric acids, but not in acetic acid.

Estimation of Lime.—In the determination of calcium for analytical purposes the oxalate is the precipitate usually employed; but before weighing it is heated to dull redness, so as to convert the oxalate into carbonate of lime: 100 parts of the carbonate contain 56 of lime. If no other base be present, calcium may also be estimated in the form of sulphate. If the calcium be not already in the state of sulphate, the salt is heated with an excess of sulphuric acid, and ignited; when cold, it is weighed: 100 grains of sulphate of lime contain 41·18 of lime.

§ IV. MAGNESIUM ($Mg=12$). *Sp. Gr.* 1·7.

(546) MAGNESIUM is usually classed with those metals the oxides of which furnish the alkaline earths, but it is much more analogous to zinc in its properties than to any other element. Magnesium is an abundant ingredient of the crust of the earth. It is found in combination in large quantities as a double carbonate with lime, forming magnesian limestone, or dolomite. It is contained abundantly in sea water as chloride, and in many springs as sulphate. It likewise enters more or less extensively into the formation of many rocks, and of a great variety of minerals.

Preparation. 1.—Bussy obtained it in the metallic form by heating its anhydrous chloride with potassium in a porcelain or platinum crucible. When cold, the contents of the vessel were digested in cold water, by which the chloride of potassium and undecomposed chloride of magnesium were dissolved out. The metal was left as a grey powder, which could be melted into globules.

2.—Deville and Caron (*Comptes rendus*, xliv. 394) obtain the metal as follows:—9000 grains of pure chloride of magnesium are mixed with 1500 grains of fused chloride of sodium and 1500 of pure fluoride of calcium, both in fine powder. 1500 grains of sodium in small fragments are carefully mingled with the powder, and the whole is thrown into a clay crucible at a full red heat, and it is then instantly covered. When the mixture has become tranquil, the cover is removed, and the fused mass is stirred with an iron rod, in order to render it homogeneous throughout, and to obtain a clean surface upon the liquid. Globules of magnesium are then distinctly visible. The crucible is allowed to cool partially, and the metallic globules are united by means of the iron rod; the melted mass is then poured upon a shovel, and the magnesium, amounting to about 675 grains, is separated from the slag. The magnesium may be placed in a porcelain tray and collected into one mass by melting it in a current of hydrogen; after which it may be purified by remelting in a bath of mixed chloride of magnesium, chloride of sodium, and fluoride of calcium.

3.—Bunsen (*Liebig's Annal.*, lxxxii. 137) prepares magnesium by the electrolytic decomposition of the chloride of magnesium; this salt he melts in a deep covered porcelain crucible divided by a vertical diaphragm of porcelain, which extends half-way down the crucible; the electrodes are made of carbon, and are introduced through two openings in the lid, the negative electrode being notched to receive the reduced magnesium which lodges in the cavities: the crucible is brought to a red heat, and is filled with the melted chloride, which then is readily decomposed by 10 cells of the zinc-carbon battery (233). The principal difficulty in this operation arises from the small density of the reduced metal, which rises to the surface of the fused salt, and is liable to reoxidation.

Properties.—Magnesium is a malleable, ductile metal of the colour of silver, which takes a high polish, and preserves it nearly as well as zinc at ordinary temperatures in dry air; but in a moist atmosphere it becomes slowly oxidized. Its fracture appears sometimes to be crystalline, at other times fibrous. It has about the same degree of hardness as calc-spar. At a moderate red heat it

may be melted. When ignited in dry air or in oxygen gas, it takes fire and becomes oxidized, emitting a light of dazzling brilliancy; the magnesia which is produced exhibits no sign of fusion. Deville and Caron have shown that magnesium is nearly as volatile as zinc, and that it may be distilled by heating it strongly in a current of hydrogen. A portion of the metal is carried away in suspension by the gas, and if the latter be kindled as it issues from the apparatus, it burns with a beautiful and highly luminous flame. Magnesium is but slowly acted upon by cold water, but it is rapidly dissolved if the water be slightly acidulated. It is also freely soluble in solutions of sal ammoniac. When thrown into strong hydrochloric acid it bursts into flame; yet a mixture of concentrated sulphuric and fuming nitric acid has no action upon it unless it be heated. When heated in chlorine and in the vapour of bromine, of iodine, or of sulphur, it burns brilliantly.

(547) MAGNESIA ($MgO=20$); *Sp. Gr.* 3·6.—The only known oxide of magnesium is a bulky, white, tasteless, infusible, and nearly insoluble powder, which when placed upon moistened turmeric paper turns it distinctly brown. 100 parts of magnesia contain 60 of magnesium and 40 of oxygen. It is usually procured by strongly igniting the artificial carbonate in a crucible, but it may also be obtained by ignition of the nitrate of magnesia; in this case it assumes a much denser form. Magnesia, when mixed with water, gradually combines with it, and forms a hydrate (HO,MgO), which absorbs carbonic acid slowly from the air: no sensible elevation of temperature occurs during the process of hydration. A native hydrate of similar composition occurs in crystalline scales.

SULPHIDE OF MAGNESIUM ($MgS=28$) is but sparingly soluble in water. It may be obtained as a hydrate by precipitating a boiling solution of sulphate of magnesia with sulphide of potassium, when it falls as a white mucilaginous mass.

(548) CHLORIDE OF MAGNESIUM ($MgCl=47{\cdot}5$; *Sp. Gr.* 2·177, *cryst.* with 6 Aq, 1·558) is contained abundantly in sea water. It may be obtained in the anhydrous condition by dissolving 1 part of magnesia in hydrochloric acid, and adding 3 parts of sal ammoniac in solution, after which the mixture is evaporated to dryness; by this means a double chloride of magnesium and ammonium is formed (H_4NCl, 2 $MgCl$), which may be evaporated without loss of acid, whilst the solution of mere chloride of magnesium is partially decomposed during evaporation: when the double salt is ignited in a covered crucible, the sal ammoniac is expelled, and pure chloride of magnesium remains. At a red heat it fuses to a transparent liquid, which forms a silky-looking mass of confused crystals on

cooling. Chloride of magnesium is deliquescent, and gives out heat whilst undergoing solution in water; by evaporation at a low temperature it may be obtained in crystalline needles with 6 Aq. It is soluble in alcohol: it forms double chlorides with the chlorides of the metals of the alkalies. If heated strongly in a current of dry ammoniacal gas, the chloride of magnesium is volatilized, and a white sublimate of $MgCl, 2\,H_3N$ is obtained (Clark).

(549) SULPHATE OF MAGNESIA ($MgO,SO_3+HO, 6\,Aq=60+63$); *Sp. Gr. anhydrous,* 2·706, *cryst.* 1·660.—This is the most important salt of magnesia. It is made in very large quantities from sea water, either by precipitating the magnesia by means of lime, and then dissolving it in sulphuric acid; or by first crystallizing out the greater part of the common salt, after which, on evaporation, crystals of the sulphate are obtained. The sulphate is also procured in considerable quantities from magnesian limestone: the rock is burned, slaked, and largely washed with water to remove part of the lime; it is then treated with sulphuric acid, and the sulphate of magnesia is separated from the sparingly soluble sulphate of lime by solution and recrystallization. It is also obtained in considerable quantity from the mother-liquors of the alum works. Sulphate of magnesia is a common ingredient in mineral waters. Its trivial name of *Epsom salts* is derived from the circumstance of its being abundantly contained in many springs in the neighbourhood of Epsom, from the waters of which it was at one time obtained. Sulphate of magnesia is soluble in 3 times its weight of water at 60°, and $1\frac{1}{3}$ at 212°. Its solution has a bitter, disgusting taste. It crystallizes readily in right rhombic prisms, which are slightly efflorescent: when heated moderately, they lose their water of crystallization; if the heat be intense and long continued, a part of the acid also escapes; 100 parts of the crystallized salt contain 48·78 of water. If crystallized from a hot solution, oblique rhombic prisms, with 6 Aq are deposited, and the ordinary crystals, when heated to 125°, become opaque and lose 1 Aq. Crystallized sulphate of magnesia loses 6 of its 7 atoms of water at a temperature below 300°, but it retains 1 atom even at 400°. This last atom may be displaced by an equivalent of an anhydrous salt, such as sulphate of potash, with which it forms a double salt, possessed of the same crystalline form as sulphate of magnesia ($MgO, SO_3+KO, SO_3+6\,Aq$) of sp. gr. 2·076. Sulphate of ammonia forms with the sulphate of magnesia a similar double salt.

NITRATE OF MAGNESIA ($MgO, NO_5+6\,Aq=74+54$; *Sp. Gr.*

1·464) is deliquescent, and soluble in alcohol; it crystallizes with difficulty.

(550) CARBONATE OF MAGNESIA ($MgO,CO_2=42$; *Sp. Gr.* 3·056) occurs native as a white, hard, amorphous mineral, called *magnesite.* It is procured artificially by precipitating a boiling solution of a salt of magnesia with carbonate of potash, and dissolving the precipitate in carbonic acid water; as the gas escapes, the salt is deposited as a terhydrate, in transparent hexagonal prisms ($MgO,CO_2 + 3\,Aq$): by exposure to air the crystals effloresce and are converted into a protohydrate (MgO,CO_2+Aq). The anhydrous carbonate may be obtained by introducing a test-tube containing a solution of sulphate of magnesia into a strong glass tube containing a solution of carbonate of soda, sealing the tube, and then allowing the two solutions to mix. Crystals of carbonate of magnesia are deposited slowly.

Magnesia alba, the common white magnesia of the shops, is made by precipitating a boiling solution of the sulphate of magnesia by a hot solution of carbonate of soda. The sulphate of magnesia is allowed to remain slightly in excess, otherwise the precipitate contains a little carbonate of soda. It is deposited as a white, light, bulky powder, which is composed of hydrate of magnesia (HO,MgO) combined with a quantity of hydrated carbonate (MgO, CO_2+Aq), the amount of which may vary from 2 to 4 atoms to 1 atom of the hydrate of magnesia; it is very sparingly soluble in water. A quantity of carbonic acid is expelled from the mixture during the preparation of this compound.

Dolomite, when its structure is crystalline, usually consists of carbonate of magnesia and carbonate of lime in the proportion of 1 atom of each ($MgO,CaO, 2\,CO_2$), though some times the proportion of carbonate of lime considerably exceeds 1 atom. A solution of sulphate of lime decomposes carbonate of magnesia at ordinary temperatures, and thus spring water originally charged with sulphate of lime may, by filtration through a bed of dolomite, become impregnated with sulphate of magnesia.

Mr. Pattinson has introduced a process by which a very pure carbonate of magnesia is manufactured from dolomite. In this operation the mineral is finely ground and sifted, and exposed to a red heat for 2 or 3 hours, by which the carbonate of magnesia is decomposed. It is then introduced into a strong iron cylinder lined with lead, where it is mixed with water, and carbonic acid gas is forced in under a pressure of 5 atmospheres, till it ceases to be absorbed; the carbonate of magnesia becomes dissolved as bicarbonate, leaving the carbonate of lime: the clear liquid, when

boiled, deposits the carbonate of magnesia, which is drained, and dried in a stove at a low temperature.

By mixing a solution of nitrate of magnesia with an excess of a saturated solution of bicarbonate of potash, and allowing the solution to stand for some days, a remarkable double salt is deposited in regular crystals, composed of [2 (MgO, CO_2) + ($KO, HO, 2\ CO_2$) + 8 Aq], but which is decomposed by re-dissolving it in water. The corresponding salt of soda is more stable.

A native *Borate of Magnesia* [2 (MgO,BO_3) + ($MgO, 2\ BO_3$)], named *boracite*, is found crystallized in cubes; it is rendered electric by heat.

(551) SILICATES OF MAGNESIA.—Silica and magnesia may be artificially combined in many proportions. A large number of minerals are formed, either wholly or partially, of the silicates of magnesia. *Olivine* or *chrysolite*, 2 (MgFe)O, SiO_2, is a crystallized mineral, usually of a green colour, obtained from basaltic and volcanic rocks; it frequently accompanies masses of meteoric iron. *Talc* is a very soft slaty mineral, which has a formula [2 (MgO, SiO_2) + 2 MgO, 3 SiO_2]. *Steatite, French Chalk*, or *Soapstone*, is (MgO, SiO_2 + 2 MgO, 3 SiO_2). *Picrosmine* is the normal hydrate 2 (MgO,SiO_2) + Aq. *Meerschaum* is another hydrated silicate, of which the formula is 2 MgO,3 SiO_2 + 4 Aq. *Serpentine* (2[(MgFe) O,SiO_2] + MgO, 2 Aq) is another hydrated silicate of magnesia, in which a portion of the magnesia is often displaced by protoxide of iron. Serpentine frequently occurs in compact masses, which take a high polish, and from the beauty of its variegated colours, it is often employed for ornamental purposes. It is readily attacked by acids, and occurs in sufficient abundance to be employed as a source of the salts of magnesia.

The double silicates of magnesia are still more numerous. *Augite* or *Pyroxene* is one of these: it is a crystalline mineral, often found in basalt and lava, and is a silicate of lime and magnesia, portions of which bases are often displaced by protoxides of iron and manganese [(CaMgFeMn)O,SiO_2]. *Hornblende* or *Amphibole* is a silicate and aluminate of magnesia, lime, and protoxide of iron, with a variable proportion of the fluorides of calcium and potassium, (3[(MgCaFe)O,SiO_2] + 2 (MgCaFeMn) O, 3 SiO_2 + H(KCa) F). It occurs sometimes in dark green or black crystals, at other times massive, disseminated through many rocks, such as syenite and porphyry, and frequently in basalt and lava. *Asbestos* and *Amianthus* commonly consist of a fibrous variety of amphibole.

(552) *Triphosphate of Magnesia and Water* (HO, 2 MgO, PO_5 + 14 Aq) is an efflorescent, sparingly soluble salt, which crystal-

lizes in fine tufts of six-sided acicular prisms, when a solution of a magnesian salt is mixed with the solution of the common phosphate of soda.

TRIPHOSPHATE OF MAGNESIA AND AMMONIA ($2\,MgO, H_4NO, PO_5 + 12\,Aq = 137 + 108$), or *triple phosphate*, as it was formerly called, is a more important compound than the foregoing one. It is prepared by mixing phosphate of soda, mingled with chloride of ammonium, with a salt of magnesia; by agitation this compound is deposited in minute crystalline grains: it furnishes a very delicate test of the presence of magnesia; it is insoluble in water containing free ammonia or muriate of ammonia, but it is taken up in appreciable quantities by pure water. It is frequently met with as a constituent of urinary calculi, both in man and in the lower animals. Phosphate of magnesia and ammonia is readily soluble in acids; ammonia precipitates it from such solutions unchanged; when ignited, it parts with its water and ammonia, and glows like alumina and zirconia as it suddenly contracts in bulk. The ignited residue contains 35·7 per cent. of magnesia, and 64·3 of phosphoric acid. It is frequently employed for the determination of the amount of magnesia.

(553) CHARACTERS OF THE SALTS OF MAGNESIUM.—The salts of magnesium are colourless, and have a bitter taste. Many of the magnesian minerals possess a silky lustre, and feel unctuous to the touch. Compounds of magnesia may be recognised *before the blowpipe*, by the pink tinge which they acquire when heated with nitrate of cobalt.

In solution they give no precipitate with the *bicarbonates of the alkalies* till boiled; but a white basic carbonate of magnesia when mixed with a neutral *carbonate of potash or soda*, unless a salt of ammonia be present, which interferes with the precipitation. *Phosphate of ammonia* gives with them a white crystalline granular precipitate of double phosphate of magnesia and ammonia, which is easily soluble in acids. *Oxalate of ammonia*, mixed with sal ammoniac, gives no precipitate with the magnesian salts, neither do the *soluble sulphates*. The *fixed alkalies* throw down a white gelatinous hydrate of the earth, which is insoluble in excess of the precipitant. *Lime water* produces a similar precipitate. *Ammonia* produces but a very incomplete precipitation of magnesia from its solutions; the gelatinous precipitate which it occasions becomes redissolved on the addition of a solution of hydrochlorate of ammonia, and a double salt of magnesia and ammonia is formed.

(554) CHARACTERS OF THE METALS OF THE FIRST GROUP (the

Alkalies).—The salts of these metals when in solution are distinguished by the following characters:—1. By the absence of any precipitate on the addition of a solution of carbonate of potash, or of soda: in the case of lithium, if the salt exceed two per cent. of the solution, a precipitate of carbonate of lithia is liable to occur. —2. By the absence of any precipitate when sulphuretted hydrogen or hydrosulphate of ammonia is added to the solution.—3. By the occurrence of a precipitate with bichloride of platinum in the case of salts of ammonium or of potassium; and by the formation of prismatic crystals of the double chloride of sodium and platinum when evaporated in the presence of salts of sodium.

(555) *Estimation of Potash and Soda.*—If the relative proportions of the potash and soda be not required, their combined weight is usually ascertained in the form of sulphates. They may in most cases be readily obtained in this condition by treating the solution with sulphuric acid, evaporating to dryness, and fusing the mass in a platinum crucible in which a fragment of carbonate of ammonia is suspended. The excess of sulphuric acid is thus readily dissipated, and the amount of the acid combined with the potash and soda is determined by precipitation with chloride of barium. When ammonia is present with salts of potash and soda, its amount may be determined by distilling off the ammonia in the manner already described (522).

In order to determine the quantity of potash and soda in a mixture of the salts of the two bases, they should be converted into the state of chlorides, and heated to low redness to expel moisture and all ammoniacal salts, allowed to cool, and weighed; a certain proportion of these mixed chlorides (ten or twelve grains will suffice) is then mixed with an excess of the bichloride of platinum, evaporated to dryness over a steam bath, and the excess of bichloride of platinum and chloride of sodium removed by washing with alcohol of specific gravity 0·860. The crystalline residue is collected on a filter and weighed. One hundred parts contain 30·53 of chloride of potassium, and correspond to 15·98 of potassium, or to 19·26 of potash. The quantity of chloride of sodium is obtained by deducting the weight of the chloride of potassium from that of the mixed chlorides employed.

(556) The conversion of the alkaline bases into the condition of chlorides, previous to precipitation by the bichloride of platinum, if they are not already in that form, is rather troublesome. They may be first converted into sulphates by evaporating the solution with a slight excess of sulphuric acid and igniting the residue; the sulphates thus obtained are to be dissolved in water and mixed

with a solution of chloride of barium in slight excess. The sulphuric acid is thus precipitated as sulphate of baryta, and the alkalies are converted into chlorides; but the excess of baryta in the liquid must still be got rid of. A mixture of caustic ammonia and of the sesquicarbonate of ammonia is therefore added to the solution after it has been filtered from the sulphate of baryta. The excess of baryta is thus thrown down as carbonate, and the carbonate of baryta may then be removed by filtration. Once more the solution is evaporated to dryness in a platinum dish, and the residue gently ignited to expel the ammoniacal salts. The remaining mass now contains nothing but the mixed chlorides of sodium and potassium.

(557) Characters of the Metals of the Second Group (Metals of the Alkaline Earths):—1. The salts of these metals when in solution give a white precipitate on the addition of solution of carbonate of soda or of potash.—2. They yield no precipitate with hydrosulphate of ammonia nor with sulphuretted hydrogen. —3. Lime-water occasions no precipitate, except in cases in which the magnesian salts are present, or in which the solution contains free carbonic acid.

(558) *Separation of the Alkaline Earths from the Alkalies.*— Supposing a solution to contain salts of the alkalies and of the alkaline earths, the quantities of each base may be determined in the following manner:—an excess of a mixture of ammonia and sesquicarbonate of ammonia is added to the solution, the liquid is filtered from the precipitate, then evaporated to dryness, and heated to expel the ammoniacal salts; the ammonia thus combines with the acid previously in union with the earths, whilst the carbonic acid converts the earths into carbonates. The dry residue is then washed with water, which dissolves out the salts of the alkalies: and from this liquid the proportions of potash and soda can be ascertained in the manner already described (555). A little magnesia is apt to accompany the salts of the alkalies: its presence may be detected and its quantity determined by the addition of lime-water to the solution; hydrate of magnesia is precipitated, and may be collected, weighed, and added to the amount obtained from the portion which was insoluble in water. The precipitation must be effected in a stoppered bottle, to exclude the carbonic acid of the atmosphere, which would precipitate a portion of lime with the magnesia. The excess of lime may be got rid of by the addition of oxalic acid, which occasions a precipitate of oxalate of lime that can be separated on a filter, but need not be weighed. The earthy carbonates must now be dealt with in the following manner:—

(559) *Separation of Barium, Strontium, Calcium, and Magnesium from each other.*—The alkalies having been separated in the manner just described, the carbonates of the earths which in the preceding operation were not dissolved by water are taken up with diluted nitric acid, and the liquid is largely diluted. Sulphuric acid is then added so long as it occasions a precipitate.

If the liquid originally contained no alkaline salts, it will not be necessary to convert the earths into carbonates, but the solution may be simply diluted, acidulated with nitric acid, and mixed with sulphuric acid, as before.

This precipitate may consist of the sulphates of baryta and strontia. It must be collected, washed with boiling water and weighed, then fused with thrice its weight of carbonate of soda, by which it will be decomposed; double decomposition occurs, carbonates of baryta and strontia, and sulphate of soda being formed. The carbonates of baryta and strontia, being insoluble, are separated from the soluble sulphate of soda by washing, and the carbonates of the two earths are converted into chlorides by the action of diluted hydrochloric acid. The chlorides of barium and strontium are evaporated to dryness, weighed, and may then be separated with tolerable exactness by the action of alcohol, which dissolves the chloride of strontium, but leaves that of barium unacted upon. Silicofluoric acid may also be employed to separate the two earths; in the course of two or three hours the whole of the baryta is precipitated by it, whilst the strontia remains in solution.

The acid liquid from which the baryta and strontia have been separated is rendered slightly alkaline by ammonia, and the lime precipitated as oxalate, by means of oxalate of ammonia: this precipitate, after being well washed, is heated to dull redness, and is estimated as carbonate of lime. If the proportion of magnesia be large, a little of the lime is retained in solution.

The filtrate, which may still contain magnesia, is mixed with phosphate of soda, briskly stirred, and allowed to stand for twelve hours, to give time for the granular crystalline phosphate of magnesia and ammonia to subside: it is collected on a filter, washed with water which contains free ammonia, and estimated, after ignition, as pyrophosphate of magnesia.

(560) It will generally be found more convenient in separating the alkaline earths from the alkalies, in the first place to precipitate the baryta and strontia by sulphuric acid from the dilute acidulated solution; then to neutralize by ammonia, and separate the lime by the addition of oxalate of ammonia; to evaporate the solution containing magnesia and the alkalies to dryness, heating,

to expel salts of ammonia; then to redissolve the residue in water, and separate the whole of the magnesia at once by the addition of lime-water in a stoppered bottle, in the manner already described.

Certain precautions in manipulation are required in transferring a solution to a filter, in order to avoid loss. In pouring a liquid from one vessel to another, a glass rod should be moistened with distilled water and brought against the edge of the vessel from which the liquid is to be poured, as shown in fig. 319. By this means, when the pouring is ended, if the rod be still kept in contact with the edge, the last drop is prevented from running down the outside of the jar or basin: the rod may then be placed in the vessel until a similar operation is again required. After the whole of the liquid has been poured off, the portion which adheres to the rod and to the sides of the vessel is washed down by a jet of water from the washing bottle, fig. 320, and the washings are added to the rest of the decanted liquid.

FIG. 319.

(561) In washing precipitates, the use of a flask provided with two tubes passing through the cork, as represented in fig. 320, facilitates the operation. The tube, *a*, passes just through the cork; the longer tube, *b*, reaches almost to the bottom of the flask; it terminates at *c* in a fine orifice; on forcing air from the lungs through the tube, *a*, the water is expelled at *c*, and may be directed upon the filter.

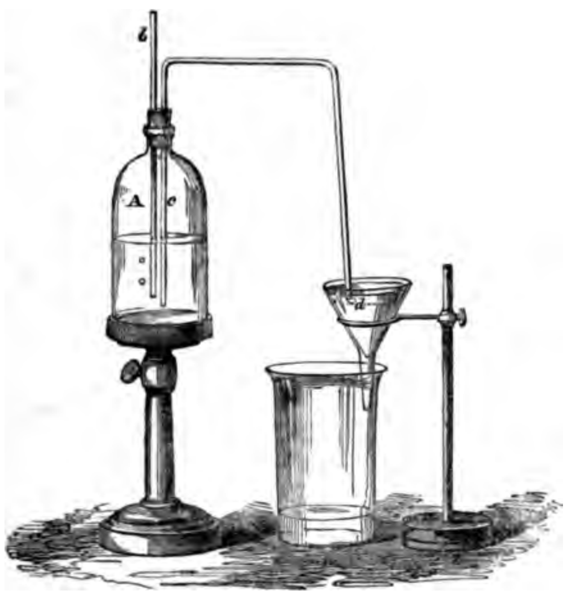
FIG. 320.

It is necessary that the filter should fall completely within the funnel, and that before any of the liquid for filtration is poured into it, the paper, after it has been placed in the funnel, should be moistened with distilled water. In washing a precipitate, the stream of water should be directed upon the upper edges of the filter, so as to wash down the saline particles, which, by evaporation of the liquid, have a tendency to accumulate there as the solution rises under the influence of capillary action.

In cases where gelatinous precipitates, like oxide of iron, or alumina, are to be washed continuously for a long period, a simple

contrivance by Gay-Lussac will be found very useful; it is merely a bottle of distilled water, A, fig. 321, which by means of a siphon, supplies the water at a regulated level in the funnel, *d*; *b* represents a tube open at both ends, which reaches nearly to the bottom of the bottle, A; *c* is a siphon with limbs of equal length, which passes a little deeper into the bottle than *b*; the limb which dips into the funnel has its lower extremity a little recurved, to direct the pure water upwards. The funnel, *d*, is placed so that the upper edge of the filter shall be a little above the level of the lower end of *c*. Under these circumstances the filter can never overflow. As soon as the surface of the liquid in the funnel falls just below the level of the lower extremity of *b*, the siphon carries over a small quantity of water, and bubbles of air rise in the bottle, A, to supply its place. This process goes on continuously as the water flows from the filter, until A is empty.

FIG. 321.



In order to ascertain whether a precipitate has been sufficiently washed, a drop of the liquid which passes through is evaporated on a slip of glass: it ought to leave no appreciable stain or residue.

In collecting a precipitate from a filter, the paper should be dried thoroughly; after which the portion that can be readily detached from the paper should be allowed to fall into the platinum or porcelain capsule in which it is intended to perform the ignition. The capsule is to be placed upon a smooth sheet of paper, and the filter being held at one corner with a pair of forceps, is burned in such a way that the ashes shall fall into the platinum capsule: any particles of ash which may fall upon the paper are carefully transferred to the capsule.

It must not be forgotten that filtering paper itself leaves traces of ash when burnt; but the amount of this in good specimens should not exceed about 3 grains in 1000. Before using any paper for the purposes of analysis, the quantity of ash (usually silica, lime, and traces of oxide of iron) which a given weight of it affords when burnt must be ascertained. In each analytical experiment the weight of the filter employed being approximatively known, it is easy to estimate the amount of ash which it would yield (at most but a few hundredths of a grain) and to deduct this from the gross weight of the precipitate.

CHAPTER XIII.

GROUP III.—METALS OF THE EARTHS.

§ I. ALUMINUM ($Al=13.7$). *Sp. Gr.* 2·5 to 2·67.

(562) THE pure earths are white, insipid, insoluble compounds, the oxides of metals which possess a high affinity for oxygen. With the exception of cerium, and lanthanum, which, with didymium, would probably be referred with greater propriety to the next group, a single oxide only of each metal of this class is known.

(563) Of these metals the most abundant and important is ALUMINUM, which derives its name from alum, into the composition of which it enters. Indeed, alumina (the oxide of aluminum) constitutes about 10 per cent. of this salt.

Preparation.—1. Aluminum was first procured by Wöhler, by decomposing chloride of aluminum in a porcelain or platinum tube by means of potassium. He obtained it first as a steel-grey powder, and subsequently in malleable globules. In the pulverulent form it is gradually oxidized by boiling water, and more rapidly by alkaline solutions. When heated in this form in oxygen gas, it takes fire and burns with a vivid light, emitting so intense a heat as to fuse the alumina, which forms a yellowish mass, in colour and hardness resembling native crystallized alumina as it exists in corundum.

2.—Bunsen obtains aluminum by the electrolytic decomposition of the double chloride of sodium and aluminum ($NaCl, Al_2Cl_3$). This salt melts at about 356°, and readily furnishes aluminum by a process similar to that already described in the case of magne-

sium: but as the aluminum is heavier than the fused salt, it is more easily collected than magnesium.

3.—The metal is now prepared upon a considerable scale, owing to improvements introduced in the method of extracting it, by Deville. He proceeds in the following manner (*Ann. de Chimie*, III. xliii. 5):—Into a wide tube of hard glass of an inch or an inch and a half in diameter, about half a pound of dry chloride of aluminum is introduced, and kept in its place by plugs of asbestos; a current of dry hydrogen, perfectly free from air, is transmitted, and the chloride of aluminum is very gently heated; in this way traces of hydrochloric acid and chlorides of sulphur and silicon are expelled. Three or four small porcelain trays, each containing 40 or 50 grains of sodium, freed from adhering naphtha by pressure between folds of blotting-paper, are then introduced into the tube; the current of hydrogen is still maintained, and heat is applied to the part of the tube which contains the sodium. This end of the tube must be slightly elevated, in order to prevent the melted chloride of aluminum from running down upon the sodium; in which case the heat emitted is so intense as to crack the tube. When the sodium is melted, the chloride of aluminum is gradually distilled over by the application of a regulated heat, and is reduced with vivid incandescence. The aluminum is condensed in the porcelain trays, in which also a double chloride of aluminum and sodium collects around the reduced aluminum. These trays and their contents when cold are withdrawn from the glass tube, and placed in a porcelain tube through which a current of hydrogen is transmitted, whilst the tube is raised to a bright red heat; the aluminum fuses into globules in the porcelain trays; and by fusing it once more in a porcelain crucible under a layer of the double chloride of aluminum and sodium, a button of pure aluminum is obtained. This process has been conducted in a reverberatory furnace upon large masses of sodium and of chloride of aluminum.

4.—Rose obtains aluminum from cryolite ($3\,NaF, Al_2F_6$) by fusing it with sodium. For this purpose Wöhler recommends 7 parts of chloride of sodium to be melted with 9 of chloride of potassium, and the mass thus furnished to be finely powdered and intimately mixed with its own weight of cryolite in fine powder. This powder is to be introduced with a fifth or a sixth of its weight of sodium (arranged in alternate layers of the powder and the metal), into a dry earthen crucible, which is to be heated rapidly in a wind furnace. An intense reaction occurs, and a portion of the sodium burns off. The mixture is next heated for about a quarter

of an hour until it is in liquid fusion, and is then allowed to cool. The aluminum generally collects at the bottom into a well-formed button, which is frequently crystalline on its surface. In some experiments the quantity of reduced metal amounted to one third of the proportion present in the mineral employed.

(564) *Properties.*—As prepared by Deville's process, aluminum is a white malleable metal, nearly resembling zinc in colour and hardness: it may be rolled into very thin foil, and admits of being drawn into fine wire; after it has been rolled, it becomes much harder and more elastic. It conducts electricity nearly as well as silver. Aluminum is remarkably sonorous, and emits a clear, musical sound when struck with a hard body. Fused aluminum crystallizes readily as it cools, apparently in regular octohedra; its point of fusion is below that of silver. It may be heated intensely in a current of air in a muffle without undergoing more than a superficial oxidation, and it is but slowly oxidized when heated to full redness in an atmosphere of steam. When thrown into fused nitre it burns with a brilliant blue light.

Nitric acid, whether concentrated or diluted, is without action upon aluminum at the ordinary temperature, and dissolves it very slowly even when boiled upon the metal. Hydrochloric acid, on the contrary, both when concentrated and when diluted, attacks it rapidly, forming chloride of aluminum, whilst hydrogen is disengaged. Solutions of the alkalies, especially when aided by heat, also attack aluminum with energy, producing alumina, which is dissolved by the alkaline solution, whilst hydrogen gas is liberated. From its lightness and inalterability in the air, aluminum has been applied to the preparation of small weights: but some difficulty is experienced in working the metal for want of a suitable solder. It is occasionally used for ornamental articles.

Aluminum readily forms alloys with copper, silver, and iron, but it may be melted with lead without any combination between the two metals taking place. Its alloys with copper are very hard, and susceptible of a high polish; they vary in colour from white to golden yellow, according to the proportion of the two metals. Aluminum also combines readily with carbon and silicon, forming greyish, granular, brittle, and crystalline compounds, which present a considerable analogy to cast iron. It does not combine with mercury.

Finely divided aluminum burns brilliantly in the vapour of sulphur, and forms a black sulphide (Al_2S_3), of semi-metallic appearance, which is rapidly decomposed by water, with formation of hydrate of alumina and sulphuretted hydrogen.

(565) ALUMINA (Al_2O_3=51·5); *Sp. Gr. of ruby,* 3·95.—This is the only known oxide of aluminum; 100 parts of it contain 53·39 of aluminum, and 46·61 of oxygen: from its isomorphism with the sesquioxide of iron, and its general resemblance to it in properties, it is regarded as a sesquioxide. It forms one of the materials that enter most largely into the composition of the superficial strata of the earth. It is the basis of all the varieties of clay, and is present in greater or less quantity in almost every soil. It occurs nearly pure, and crystallized in six-sided prisms, in *corundum,* in which mineral it has a specific gravity of 3·95, and is hard enough to cut glass. The *sapphire* and the *ruby* are also composed of this earth, tinged with a small quantity of oxide of chromium. They are only inferior to the diamond in hardness. *Emery,* which from its hardness is so largely used in grinding and polishing, after it has been powdered and levigated, is another form of alumina, coloured with oxides of iron and manganese.

In order to obtain alumina, it is sufficient to ignite pure ammonia alum ($H_4NO,SO_3+Al_2O_3,3SO_3+24Aq$) intensely for some time; the water, ammonia, and sulphuric acid escape, and anhydrous alumina is left, in the proportion of 11·34 parts of alumina for 100 of the crystallized salt. It is, however, nearly impossible to expel the last portions of sulphuric acid, as the salt swells up enormously, and forms a white, porous, infusible mass, which is an extremely bad conductor of heat. Alumina may also be procured from alum quite free from iron; the salt should be dissolved in water and precipitated by carbonate of potash in slight excess: the liquid should be warmed, and the precipitate well washed; but since traces of potash always adhere to it obstinately, it must be redissolved in hydrochloric acid, and then thrown down by ammonia or carbonate of ammonia; in which case it falls as a white semi-transparent, bulky, gelatinous hydrate, which must be again thoroughly washed. In this form alumina is completely soluble in a solution of potash, and is readily taken up by acids. On drying, it contracts very much, and forms a yellowish, translucent mass, like gum, retaining 3 Aq. *Diaspore* is a natural hydrate (Al_2O_3+Aq), which decrepitates strongly when heated, and falls to powder.

The hydrate of alumina when ignited loses its water, and at a certain temperature presents an appearance of sudden incandescence; it contracts greatly at the moment that this effect is produced, and is afterwards nearly insoluble in acids. Hydrate of alumina is strongly hygroscopic, and adheres to the tongue when applied to it.

Alumina fuses before the oxyhydrogen blowpipe, and yields a colourless, transparent mass, resembling corundum. Gaudin states that artificial crystals, having the form and hardness of the ruby, may be obtained by calcining equal parts of sulphate of potash and alum, and introducing the mixture in fine powder into a crucible lined with lampblack. The cover is then to be luted on, and the crucible exposed to the highest heat of a forge for a quarter of an hour. In this operation the sulphuric acid of the sulphate of alumina is expelled, the sulphate of potash is reduced to sulphide of potassium, and this compound dissolves a portion of the liberated alumina, depositing it in minute prismatic colourless crystals, during the slow cooling of the mass. These crystals may be cleansed from adhering impurities by digestion in dilute aqua regia. Similar crystals have also been obtained by Deville, who has succeeded in imitating the hue both of the ruby and the sapphire. Alumina forms salts with the more powerful acids, but these salts are readily decomposed: they all have an acid reaction; and indeed alumina possesses properties which approach somewhat to those of an acid, for it has a strong tendency to unite with basic oxides. The *spinelle ruby*, for example, is a native aluminate of magnesia (MgO, Al_2O_3), and *gahnite* is an aluminate of zinc (ZnO, Al_2O_3). Fremy has also obtained a white granular compound of alumina with potash, to which he assigns the formula (KO, Al_2O_3). When the solution of alumina in potash is exposed to the air it absorbs carbonic acid, and a terhydrate of alumina is deposited in regular crystals.

Alumina when combined with silica forms clay, which is the basis of porcelain and of earthenware. To the dyer and the calico printer the compounds of alumina are of high value: the hydrate of alumina has the property of combining intimately with certain kinds of organic matter, and when salts of alumina are mingled with coloured vegetable or animal solutions, and precipitated by the addition of an alkali, the alumina carries down the greater portion of the colouring matter, forming a species of pigments termed *lakes*. By soaking the cloth with a preparation of alumina, the earth attaches itself to the fibre; and if cloth thus prepared be plunged into a bath of the colouring matter, it becomes permanently dyed. Most colouring matters would be removed by washing, were it not for the intervention of some *mordant*, or substance which thus adheres to the fibre as well as to the colouring matter. Binoxide of tin and the sesquioxides of iron and chromium resemble alumina in this respect, and are largely used as mordants in dyeing calicoes and woollens.

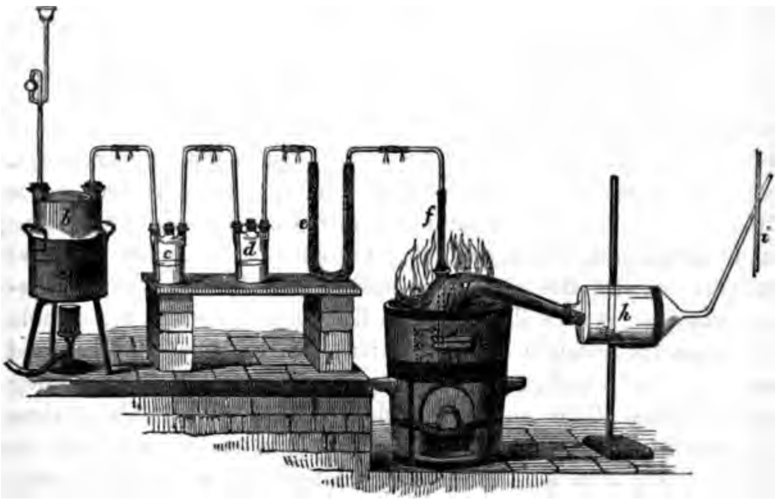
Mr. Crum (*Q. J. Chem. Soc.*, vi. 216) has described a remarkable modification of hydrate of alumina, which, in the presence of a very small proportion of acetic acid, is largely soluble in water, and is coagulated and rendered insoluble by a minute trace of sulphuric acid. It appears to be probable from the experiments of Péan de St. Gilles (*Chem. Gaz.*, 1855, p. 165) that sesquioxide of iron admits of a similar modification: these compounds will be further alluded to when the salts of acetic acid are described (1169).

(566) Chloride of Aluminum ($Al_2Cl_3=63$); *Sp. Gr. of Vapour*, 9·34.—The anhydrous chloride of aluminum cannot be formed directly by dissolving alumina in hydrochloric acid and evaporating to dryness; since during the expulsion of the water a great part of the acid is also driven off. It may be procured as a yellow, anhydrous, volatile sublimate, by a process devised by Oersted:—alumina, mixed with charcoal powder, is made up into paste with starch or oil, and subdivided into pellets: these pellets are charred in a covered crucible, and then exposed to ignition in a current of dry chlorine. In this operation, carbon, in a very finely divided state, is mixed with the alumina: when the mass is heated with chlorine the carbon unites with the oxygen of the alumina, and the chlorine seizes the liberated aluminum; $Al_2O_3+C_3+Cl_3=Al_2Cl_3+3\,CO$. The chloride of aluminum condenses in the cool part of the tube in a crystalline, somewhat translucent mass, or as an amorphous powder.

In preparing the chloride of aluminum, an apparatus similar to that shown in fig. 322 may be used: *b* is a vessel containing a mixture of black oxide of manganese and hydrochloric acid, for generating chlorine; *a* is a water-jacket, for applying a moderate heat; *c* is a wash-bottle containing water; *d* contains sulphuric acid; *e* is a bent tube filled with pumice-stone soaked with oil of vitriol, to remove the last traces of moisture; *g* is an earthen retort, filled with the mixture of charcoal and alumina, heated by a charcoal fire. The chlorine is conveyed nearly to the bottom of this retort by means of a porcelain tube, *f*, luted into the tubulure: the gas re-acts upon the mixture in the retort, forming carbonic oxide and chloride of aluminum; and the chloride of aluminum condenses in the gas-jar, *h*, which is placed for its reception: the open mouth of this jar is closed by means of a funnel, luted on with a strip of pasted paper; and the carbonic oxide escapes through the open tube, *i*, into the chimney. In order to purify the crude chloride of aluminum from the small quantity of volatile perchloride of iron which usually accompanies it, the compound is redistilled from

iron wire, by which the perchloride of iron is converted into protochloride, which is not volatile, and the chloride of aluminum sublimes in a state of purity.

FIG. 322.



Deville prepares this chloride on a large scale from a mixture of coal tar and alumina, which is heated in a clay retort, such as is used in gas making; a current of chlorine is sent over the ignited mass, and the product of the operation is received in a chamber lined with glazed brickwork.

If chloride of aluminum be heated in considerable mass, it melts at a dull red heat, and near its fusing point sublimes rapidly; when exposed to the air it emits fumes of hydrochloric acid: it is very deliquescent, and when thrown into water hisses from the heat developed by the violence of the combination. This solution, when concentrated by a very moderate heat, yields crystals with 12 Aq. It is soluble in alcohol. By subliming chloride of aluminum in a current of sulphuretted hydrogen it forms a combination with this gas: this compound is decomposed by resublimation, or by solution in water. The chloride may also be made to combine with phosphuretted hydrogen, and with ammonia.

FLUORIDE OF ALUMINUM occurs native, combined with fluoride of sodium, forming *cryolite* ($3\ NaF + Al_2F_3$). It may be obtained in large quantity from Greenland, and as it is easily decomposed by sodium, it has been employed as a source of metallic aluminum. Another highly prized aluminous mineral, containing fluorine, is the *topaz*, which is extremely hard; the colourless

variety of it has a lustre which has sometimes caused it to be mistaken for the diamond. Its composition is represented by the formula [2 (Al_2O_3, SiO_2) + Al_2O_3, SiF_2].

(567) SESQUISULPHATE OF ALUMINA (Al_2O_3, $3\,SO_3 + 18\,Aq = 171{\cdot}5 + 162$).—This salt is formed by dissolving alumina in sulphuric acid. It is now manufactured on a large scale in the north of England, by mixing finely-powdered clay or shale, after it has been gently roasted, with about half its weight of crude sulphuric acid from the chambers, heating it gradually until fumes of acid begin to escape; this digestion is continued for 3 or 4 days, after which the mass is lixiviated, and the solution thus obtained is freed from iron by the addition of ferrocyanide of sodium so long as it occasions a blue precipitate; the clear liquid is decanted and evaporated, and the residue is sold under the name of *concentrated alum*. It crystallizes in thin flexible scales which are soluble in twice their weight of cold water: this solution may be used as a test for potash, for by mixing it with a solution containing a salt of this alkali, and evaporating, octohedral crystals of alum are deposited. Sulphate of alumina has a strong tendency to form double salts with monobasic sulphates, of which those with the sulphates of potash and ammonia, constituting potash and ammonia alum, respectively, are the most important. A remarkable anhydrous sulphate of alumina which assumes the form of a white mealy powder, insoluble in cold water, but which may be rendered soluble, and converted into the ordinary sulphate, by prolonged boiling, is obtained by boiling cryolite, or ordinary alum, with from three to ten times its weight of oil of vitriol, and distilling off about three fourths of the sulphuric acid; the bisulphate of potash, or of soda, may be removed by washing, and the anhydrous sulphate is left as a white powder, analogous to the corresponding modification of the sesquisulphates of iron and chromium (Persoz).

(568) ALUM; *Sulphate of Alumina and Potash* ($KO, SO_3 + Al_2O_3, 3\,SO_3 + 24\,Aq = 258{\cdot}5 + 216$); *Sp. Gr. anhydrous*, 2·228, *crystallized*, 1·726.—This valuable salt is occasionally found native in volcanic districts in the form of a white efflorescence, produced by the action of the sulphuric acid of the volcano upon the alumina and potash contained in the lava and trachytic rocks. For the purposes of commerce, however, alum is manufactured artificially. Three principal methods are adopted:—

1.—In the first the alum is procured by the addition of sulphate of potash to the crude sulphate of alumina prepared from clay by the process just described.

2.—A still simpler method is practised in Italy, where, especially in the neighbourhood of Civita Vecchia, the *alum-stone* is abundant. This rock contains the elements of alum, with an excess of hydrate of alumina, mixed with a variable proportion of siliceous matter. The ore is first roasted at a gentle heat in kilns, avoiding direct contact with the fuel: water is thus expelled, and the mass is rendered spongy; the hydrate of alumina is decomposed, and the formation of a basic sulphate of alumina and potash, which is insoluble in water, is thereby prevented: the roasted ore is then arranged in long heaps or ridges upon a firm clay floor, where it is frequently moistened with water: in the course of two or three months, the mass crumbles down into a sort of mud, which is lixiviated; and the solution when evaporated yields crystals of alum, which after a second crystallization are fit for the market. This variety of alum, known as *Roman alum*, crystallizes in opaque cubes, which retain subsulphate of alumina.

3.—A third process is resorted to in England and Germany for the purpose of turning alum schist, or *alum ore* as it is termed, to good account. This mineral is abundant at Whitby, in Yorkshire, and in the neighbourhood of Glasgow: it is a bituminous shale, found amongst the lower beds of the coal measures, and it contains a large quantity of very finely divided iron pyrites, disseminated through its mass, which is composed chiefly of a siliceous clay. The mineral is decomposed either by exposure to the air, or, as is more usually practised, by a slow roasting, conducted upon the ore arranged with alternate layers of fuel in long heaps or ridges, which are covered more or less completely with spent ore, in order to regulate the heat and to absorb the excess of sulphuric acid. In this operation the pyrites, or bisulphide of iron, is converted into the protosulphide of iron, losing half its sulphur, which absorbs oxygen and is converted into sulphuric acid; this acid unites with the alumina, while the protosulphide of iron, gradually combining with more oxygen, is converted into protosulphate of iron, or green vitriol; $FeS_2 + O_3 = FeS + SO_3$; and $FeS + O_4 = FeO,SO_3$. Great care is required to prevent the temperature from rising too high, a circumstance which would be attended with decomposition of the sulphate of alumina and loss of sulphuric acid. By the time that the roasting is complete, the mass has become greatly reduced in bulk, and is rendered porous and freely permeable to the air; in this condition the heap is allowed to lie exposed to the atmosphere, and is moistened from time to time; it is then lixiviated, the liquor is digested on metallic iron to reduce any persalt of the metal to the state of protosulphate,

and the protosulphate of iron is separated from the sulphate of alumina by crystallization of the liquor. The mother-liquors often yield sulphate of magnesia when concentrated further.

In the Whitby alum works, in which the quantity of the sulphate of alumina much exceeds that of the sulphate of iron in solution, the concentration is completed in leaden pans; being carried so far as that the liquid shall, when cold, be perfectly saturated, but shall deposit no crystals. The liquid is then run off into the precipitating tank, where it is mixed with a saturated solution of sulphate of potash, or, still better, of chloride of potassium, in quantity sufficient (as found by trial on the small scale) to yield the maximum proportion of alum. The mixture is briskly agitated, and the double sulphate of alumina and potash, which is sparingly soluble in cold water, is deposited in minute crystals, technically termed *alum meal* or flour. When chloride of potassium is used the sulphate of iron is decomposed, sulphate of potash is produced, and the very soluble protochloride of iron is retained in the liquor; $KCl + FeO,SO_3 = KO,SO_3 + FeCl$. To produce 100 parts of crystallized alum, between 18 and 19 parts of sulphate of potash are required, or about 16 parts of the chloride of potassium. The mother-liquor is drained off and preserved, and the crystals, which have a reddish-brown colour from adhering iron, are twice washed by subsidence with a small quantity of cold water, being well drained after each washing. The crystals are then dissolved by heat in as small a quantity of water as possible, and the solution is run off into crystallizing barrels, which in ten days or a fortnight are taken to pieces; the crystalline mass is broken into fragments, drained, and sent into the market.

In the Scotch alum works at Campsie, in the neighbourhood of Glasgow, alum meal is not formed; but the hot liquor from the evaporating pan is run into a stone cooler, in which the necessary quantity of dry chloride of potassium has been placed. The liquid is thoroughly agitated and left to cool; on the sides of the vessel large crystals of alum are formed in four or five days. The mother-liquor is then drained off, and the crystals are afterwards washed and recrystallized twice.

Where sulphate of ammonia can be obtained sufficiently cheap, it may be substituted for sulphate of potash in the manufacture of alum, as the double salt which it forms with sulphate of alumina crystallizes with almost as much facility as the potash salt; it constitutes what is known as *ammonia alum*. Indeed, for the purposes to which alum is applied, neither the sulphate of potash nor that of ammonia is essential; the object proposed in the manu-

facture of alum being to obtain a salt of alumina which, by the facility with which it crystallizes, can be freed from iron and from earthy impurities.

A number of other salts may be procured which have the same crystalline form as potash alum, and are similar to it in constitution: thus, sulphate of potash may be displaced by sulphate of soda, and a soda alum may be formed, but the compound is much more soluble than potash alum : in like manner the place of the sesquisulphate of alumina may be supplied by sesquisulphate of iron, of chromium, or of manganese, forming a remarkable series of isomorphous compounds, some of which are enumerated in the annexed table:—

Potash alum . .	$KO,SO_3 + Al_2O_3, 3\,SO_3 + 24\,Aq$
Ammonia alum .	$H_4NO,SO_3 + Al_2O_3, 3\,SO_3 + 24\,Aq$
Soda alum . . .	$NaO,SO_3 + Al_2O_3, 3\,SO_3 + 24\,Aq$
Iron alum . . .	$KO,SO_3 + Fe_2O_3, 3\,SO_3 + 24\,Aq$
Chrome alum . .	$KO,SO_3 + Cr_2O_3, 3\,SO_3 + 24\,Aq$
Manganese alum .	$KO,SO_3 + Mn_2O_3, 3\,SO_3 + 24\,Aq$.

Besides these true alums, a number of double salts of alumina may be formed with the sulphates of the oxides isomorphous with magnesia, which crystallize in fine silky needles. A native sulphate of alumina and manganese was found by Kane and by Apjohn to contain 25 equivalents of water, for which Graham proposes the formula, $MnO, SO_3, HO + Al_2O_3, 3SO_3 + 24\,Aq$, representing a compound of 1 equivalent of the sulphate of manganese with its equivalent of constitutional water, in combination with the tersulphate of alumina. A similar salt of iron has been met with in the native state.

Ordinary alum has a sweetish, astringent taste; it is soluble in about 18 parts of cold water, and in less than its own weight of boiling water. The solution has a strongly acid reaction, and dissolves iron and zinc with evolution of hydrogen. When heated, this salt first melts in its water of crystallization, which amounts to 45·43 per cent. of its weight; as it loses water it froths up, and forms a tough, tenacious paste, which is ultimately converted into a voluminous, white, infusible, porous mass of anhydrous or *burnt alum*. If crystallized alum be submitted to a regularly increasing heat, a certain proportion of the water contained in it is readily driven off: thus by a temperature of 212°, 10 equivalents out of the 24 are expelled, and 10 more at 248°. If the salt be now heated to 392°, it is rendered anhydrous and insoluble in water (Gerhardt). By ignition, alum loses a great part of its acid.

Alum is largely employed in dyeing: when used in this process its solution is gradually mixed with carbonate of soda, so long as the precipitate is redissolved on agitation, which happens till two thirds of the acid have been neutralized. The salt employed, therefore, is a solution of $Al_2O_3,SO_3 + KO,SO_3 + 2\ (NaO,SO_3)$. Cloths dipped into this liquid remove the alumina thus redissolved, and contract an intimate mechanical combination with it, by which they are enabled, as already mentioned, to retain the colours of the dye stuffs employed. Upon evaporation, cubic crystals of alum are deposited from this solution, and the excess of alumina separates. A hydrated subsulphate of alumina (Al_2O_3, $SO_3 + 9$ Aq), containing the same proportion of sulphuric acid and alumina as that formed in the mordanting liquid just described, is obtained by precipitating the sesquisulphate of alumina incompletely by caustic ammonia; it is a white insoluble powder. A white earthy-looking mineral, termed *aluminite,* said to have the same composition as this subsulphate, is found near Newhaven.

(569) PHOSPHATES OF ALUMINA.—Several minerals occur, into the composition of which phosphate of alumina enters. The blue *turquoise* is a hydrated native phosphate, $2\ Al_2O_3,\ PO_5 + 5$ Aq, coloured by oxide of copper and oxide of iron. *Gibbsite,* which was formerly considered to be a hydrate of alumina, was found by Hermann to consist of a hydrated phosphate of the earth, mixed with variable proportions of hydrate of alumina. Phosphate of alumina ($Al_2O_3,\ PO_5$) may be prepared artificially by mixing a solution of phosphate of soda with one of alum; the precipitate must be well washed. If this precipitate be redissolved in an acid, and ammonia be added, the precipitate thus occasioned has, according to Rammelsberg, the composition ($4\ Al_2O_3,\ 3\ PO_5 + 18$ Aq). *Wavellite* is a mineral which crystallizes in radiating tufts of needles; according to Berzelius, it is a combination of fluoride of aluminum with the last mentioned subphosphate of alumina, $3\ (4\ Al_2O_3,\ 3\ PO_5 + 18\ Aq) + Al_2F_3$. The mineral *amblygonite* is a combination of the same subphosphate of alumina with phosphate of lithia ($2\ LO,PO_5 + 4\ Al_2O_3, 3\ PO_5$). *Lazulite,* $2\ (3\ [Ca\ MgFe]\ O,PO_5) + (4\ Al_2O_3,\ 3\ PO_5) + 6$ Aq), is a blue mineral composed of another double phosphate which contains the same phosphate of alumina, coloured by subphosphate of iron (Rammelsberg).

Phosphate of alumina, in its hydrated form, is readily soluble in hydrochloric acid. Its solution may be precipitated by potash, but the precipitate is redissolved by an excess of the alkali. In the operations of analysis it is often necessary to separate phosphoric acid from alumina: this is most readily effected by Chancel's

method, in which the solution in nitric or acetic acid, perfectly freed both from hydrochloric and sulphuric acid, is mixed with an acid solution of nitrate of bismuth (370). Phosphoric acid is thus precipitated as the phosphate of bismuth (BiO_3,PO_5), and the whole of the alumina remains in solution.

(570) SILICATES OF ALUMINA.—The compounds of silica with alumina are numerous and important. All the varieties of clay consist of hydrated silicate of alumina more or less mixed with other matters derived from the rocks which, by their disintegration, have formed the clay. Clay is, in fact, the result of the combined action of air and water upon felspathic and siliceous rocks, and therefore necessarily varies considerably in composition. The fundamental constituent of the more important varieties of clay, according to the researches of Brongniart, of Malaguti, and others, is represented by the formula $Al_2O_3, 2\ SiO_2 + 2\ Aq$. This appears to be the composition of the fire-clay of the Staffordshire coal measures. The ordinary varieties of clay, however, contain fragments of undecomposed rock, a certain proportion of potash, and variable amounts of silica in the hydrated condition, mixed with oxide of iron, lime, and magnesia; the character of the clay is materially modified according as one or other of these ingredients predominates.

Pure clay, before it has been ignited, forms, when kneaded, a tenacious, plastic paste, which is insoluble in water, but may readily be diffused through it in particles which are in an extreme state of subdivision; the deposit, when freed from the excess of water, as it subsides, resumes its plastic character. This paste, when slowly dried, and exposed to a high temperature, shrinks very much, and splits into masses which are extremely hard, but they do not undergo fusion in the furnace. Pure hydrated silicate of alumina is very slowly acted upon by hydrochloric or by nitric acid; but it is decomposed when heated with concentrated sulphuric acid; and upon this fact one of the processes for preparing alum (568) is founded. A gentle roasting of the clay, previous to the addition of the acid, frequently favours its disintegration; but ignition at a high temperature renders it proof against the action of all acids. Strong solution of potash dissolves unburnt clay very slowly; but if alkali in excess be fused with clay, the resulting mass is rendered easily soluble in water.

The intermixture of lime, magnesia, or oxide of iron, in any considerable quantity, with the clay, greatly increases its fusibility, diminishes its plasticity, and causes it to be more readily attacked by acids: whilst an excess of silica renders it less fusible.

Clay emits the peculiar odour known as argillaceous when breathed upon or slightly moistened: its presence in any soil may be roughly but readily distinguished by the absorbent quality which it exhibits when applied in a dry state to the tongue or the lips; it adheres to them strongly, and absorbs the saliva from their surface. This absorbent property of clay causes it to retain ammonia in the soil to an extent which is of great importance to growing plants, and, as Way has shown, it arrests the ammoniacal portions of the manure applied to the surface, and thus not only ministers to the growth of the crop, but exerts a very important purifying influence upon water impregnated with organic and other substances, which find their way slowly through the soil. Indeed, mere agitation of such water with finely divided clay is sufficient to remove a considerable amount of the organic and saline matter previously in solution. It was found that both sulphate of ammonia and chloride of ammonium were partially decomposed by the lime of the clay, the ammonia being retained, whilst a corresponding amount of sulphate of lime or of chloride of calcium was formed in the solution. A similar decomposing action was also exerted by clay upon nitrate of potash.

(571) *Varieties of Clay.*—The most important varieties of clay are the following:—

1.—The celebrated *kaolin*, or porcelain clay of China, is a very pure white clay, which is furnished by the decomposition of a granitic rock, the constituents of which are quartz, felspar, and mica, the felspar having gradually mouldered into this substance. A very similar description of clay is obtained near St. Austel, in Cornwall, and at St. Yrieix, near Limoges, in France. It is in these cases chiefly produced by the disintegration of a rock known to geologists as *pegmatite*, which is, in fact, a species of granite in which mica is almost wanting, and quartz present in but small quantity. The *Cornish stone* used by the porcelain makers is the same rock in a less advanced stage of disintegration. The plasticity of kaolin is much less than that of the clay derived from disintegration of the secondary rocks.

2.—*Pipeclay* is a white variety of clay, which is nearly free from iron. That of the Isle of Purbeck, in Dorsetshire, where it occurs nearly at the base of the clay deposits, is preferred; it is used in the manufacture of tobacco pipes without any addition; before the oxyhydrogen blowpipe it melts to a transparent, nearly colourless glass.

3.—The *blue clay* of Devonshire and Dorsetshire is highly prized, as it is eminently plastic. The organic matter to which it

owes its colour is destroyed when heated, and it yields a white paste when fired. It is employed as one of the materials in the manufacture of porcelain. The upper beds of this clay frequently contain a large proportion of sand mixed with the plastic material, and are well suited for making salt-glazed stoneware without further admixture.

4.—When the proportion of carbonate of lime in a clay is considerable, it constitutes what is known as a *marl;* if the aluminous constituent preponderate, it forms an aluminous marl; if the carbonate of lime be in excess, it is a calcareous marl. The aluminous marls are extensively used in the manufacture of the coarser and more porous kinds of pottery.

5.—*Loam* is a still more mixed substance, belonging to the more recent alluvial formations; it is the common material of which bricks are made; its red or brown colour is derived from the large proportion of peroxide of iron which it contains.

6.—*Yellow ochre* and *red bole* are clays which derive their colour from oxide of iron, which is present in them in large quantity.

Halloysite is a white hydrated silicate of alumina which greatly resembles kaolin in appearance, but it is destitute of any plastic character, and is therefore unfitted for the manufacture of porcelain. *Fuller's earth* is a porous silicate of alumina which has a strong adhesion to oily matters: if made into a paste with water, and allowed to dry upon a spot of grease upon a board or a cloth, it removes most of the oil by capillary action. Amongst other localities in England it is found abundantly near Reigate, in Surrey.

The following table exhibits the composition of some of the more important varieties of clay used in the arts. The first two are results obtained by Ebelmen and Salvetat, the others are from analyses executed in Richardson's laboratory, and are quoted in the second volume of the English translation of Knapp's *Technological Chemistry* :—

	Washed kaolin.			Stourbridge fire-clay.	Pipe-clay.	Sandy clay.	Blue clay.	Brick clay.
	Chinese.	St. Yrieix.	Cornish.					
Silica . .	50·5	48·37	46·32	64·10	53·66	66·68	46·38	49·44
Alumina .	33·7	34·95	39·74	23·15	32·00	26·08	38·04	34·26
Oxide of iron	1·8	1·26	0·27	1·85	1·35	1·26	1·04	7·74
Lime . . .	...	...	0·36	...	0·40	0·84	1·20	1·48
Magnesia .	0·8	trace	0·44	0·95	trace	trace	trace	5·14
Potash and soda .	1·9	2·40	12·67 (potash, soda and water)					
Water . .	11·2	12·62		10·00	12·08	5·14	13·57	1·94
	99·9	99·60	99·80	100·05	99·49	100·00	100·23	100 00

Besides these amorphous silicates of alumina, there are many which occur in a crystalline form. *Disthene,* or *cyanite,* is a blue-coloured soft mineral of this kind (Al_2O_3,SiO_2).

Other aluminous Minerals.—The *zeolites* are hydrated double silicates in which the principal bases are alumina and lime. They boil up when heated upon charcoal before the blowpipe, and are dissolved by acids, leaving the silica in a gelatinous state. In these minerals the lime is liable to displacement more or less complete by protoxide of iron, by magnesia, or by the alkaline bases. They are often very beautifully crystallized. *Analcime* ($NaO, SiO_2+Al_2O_3, 3\ SiO_2+2\ Aq$) is one of these minerals; it crystallizes in cubes. *Stilbite* crystallizes in radiated needles, and has the composition of hydrated labradorite, ($CaO, 3\ SiO_2+Al_2O_3, 3\ SiO_2+6\ Aq$). *Prehnite* crystallizes in six-sided prisms; it may be represented by the formula, $2\ (CaO,SiO_2)+Al_2O_3,SiO_2+Aq$.

The varieties of *felspar* ($MO, 3\ SiO_2+Al_2O_3, 3\ SiO_2$) are likewise double silicates of alumina with potash, soda, lithia, or lime. Potash-felspar, the *adularia* or *orthoclase* of mineralogists, and the *petuntze* of the Chinese potters, is sufficiently hard to scratch glass; it is used as a glaze in the manufacture of the finest kinds of porcelain. Felspar requires the most intense heat of the porcelain furnace for its fusion, when it forms a white milky glass. Soda-felspar, from its usual white colour, has received the name of *albite.* The felspar containing lithia constitutes *petalite.* Common, or potash-felspar, crystallizes in oblique rhombic prisms. *Labradorite* is a double silicate of alumina, analogous to felspar, but it contains lime instead of the alkaline bases: it crystallizes in doubly oblique prisms belonging to the sixth system.

These minerals, by disintegration, yield the porcelain clay, or kaolin.

Felspar not only forms the regularly crystallized minerals just mentioned, but it occurs mingled with quartz and other crystallized minerals: it is indeed one of the most abundant constituents of many of the older rocks. *Granite,* for example, is a rock consisting of intermixed crystals of quartz, felspar, and mica. When it contains hornblende instead of mica, the term *syenite* is given to it. *Gneiss* contains the same components as granite, but it has a more stratified appearance, as the mica occurs more in layers. *Porphyry* consists chiefly of compact felspar, with crystals of felspar disseminated through it; it is often red or green, and takes a fine polish. *Basalt* is a dark-coloured volcanic rock, consisting of compact felspar containing crystals of augite. When the place of the felspathic constituent is supplied by

labradorite (or lime-felspar), the basalt is called *dolerite*. *Trap*, or *greenstone*, is a very tough, compact, igneous rock, of a dark greenish or brownish-black colour; it is composed of an intimate mixture of felspar and hornblende. If it contain soda-felspar (albite), the rock is known under the name of *diorite*. *Trachyte* is a volcanic rock also consisting chiefly of felspar, less compact than either porphyry or basalt. The porous *pumice-stone* of volcanic districts is probably altered felspar; it contains a much smaller proportion of alkali than the crystallized mineral. Melted pumice constitutes *obsidian*, or volcanic glass.

Garnet, which commonly crystallizes in rhombic dodecahedra, and *idocrase*, which crystallizes in square prisms, are basic double silicates of lime and alumina, in which part of the lime is displaced by other protoxides, and the alumina by sesquioxide of iron [3 (CaMgFeMn)O, 2 SiO_2 + $(AlFe)_2O_3$,SiO_2]. In *pyrope*, which is a species of garnet found in Bohemia, the colouring matter is partly sesquioxide of chromium. These minerals have a hardness greater than that of quartz.

The different forms of *mica* are also double silicates of alumina, which contain in addition a small quantity of water and some alkaline fluoride. *Uniaxal* mica consists chiefly of silicate of magnesia and silicate of alumina, 2 [2 (MgKFe)O,SiO_2] + $(AlFe)_2O_3$, 2 SiO_2. In *biaxal* mica (KFe)O, 3 SiO_2 + 3 [$(AlFe)_2O_3$,SiO_2], on the other hand, silicate of potash predominates. *Lepidolite* is a variety of biaxal mica in which silicate of lithia takes the place of silicate of potash.

Another important double silicate of alumina and magnesia constitutes *chlorite* [4 (MgFe)O,SiO_2 + $(AlFe)_2O_3$,SiO_2 + 3 Aq], which occurs both massive and in crystals with a granular fracture; it is of a green colour. In the massive form of chlorite slate it occurs as one of the primitive rocks which is widely distributed. There are many varieties of slate. *Roofing slate* is an argillaceous rock which splits readily into thin laminæ. *Mica slate*, as its name implies, contains particles of mica, to which it owes its glistening appearance. *Hornblende slate* contains hornblende in place of mica, and has little lustre.

(572) *Porcelain and Pottery Ware*.—In the preparation of earthenware the material employed is required to possess a plasticity equal to that of red-hot glass, and yet to be capable of being rendered by heat sufficiently firm and hard to resist the mechanical violence necessarily inflicted on it by daily use.

The basis of earthenware porcelain and china is silicate of

alumina; it possesses the plasticity required, and when heated assumes a great degree of hardness. Pure silicate of alumina, however, contracts greatly and unequally on drying: the utensils made from it would consequently be liable to crack during their desiccation; in order, therefore, to diminish the amount of this contraction, an addition of some indifferent powder, such as ground flint, is made; while to compensate for the loss of tenacity thus occasioned, and which is particularly experienced in the use of the fine clays employed for porcelain, some fusible material is added, which, at the temperature required for firing, undergoes vitrification, and greatly assists in binding the mass together. According to the greater or less proportion of these fusible materials, the ware is more or less semi-transparent, and more or less subject, like glass, to fly on the application of sudden changes of temperature.

The articles which have passed once through the kiln, and have thus acquired firmness, are rough and uneven, and the coarser kinds of ware are very porous. It is usual, after the first firing, in order to give smoothness and uniformity to the surface, as well as to render the body of the ware impermeable to moisture, to cover it with a kind of flux or glaze, which melts at a lower temperature than the material composing the ware itself; and in order to melt the glaze the articles are a second time passed through the kiln.

The materials employed in the fabrication of porcelain and earthenware are, clays of various degrees of purity and fineness, ground felspar, calcined flints or sand, burnt bones, chalk, and carbonate of soda or of potash; they do not, therefore, differ very greatly from those which are employed in glass-making, except in the great preponderance of silicate of alumina. The varieties of pottery or earthenware are numerous: the following include those which are of most importance:—

1.—*Porcelain*, or *China*.—This is the finest and most valuable description of ware: it is distinguished from ordinary earthenware by the composition of the paste from which it is formed. The materials are selected with great care, in order that they may give a colourless mass after firing. Porcelain consists mainly of two classes of materials, one of which, the clay, is plastic, and is infusible at the temperature employed to fire it; the other (chiefly silicate of lime and potash) softens and becomes vitrified, forming a kind of cement which binds the clay firmly together, and thus produces a translucent mass, which when broken appears to be of a uniform texture throughout, and is impervious to liquids. Much

judgment is required in the due proportioning of the fusible and infusible materials.

The celebrated Sèvres porcelain resembles the original Chinese ware, of which indeed it is an imitation. Regnault states the composition of the paste used at Sèvres for ornamental purposes to be the following:—Washed kaolin, 62 parts: Bougival chalk, 4; Aumont sand, 17; quartzose felspar, 17. These ingredients are carefully levigated and then thoroughly incorporated. As however the composition of the kaolin varies, the proportion of the other materials is necessarily varied likewise, so as to obtain a porcelain of uniform composition.

In order to give a smooth surface to the ware, a glaze similar in composition to the fusible material is used. The glaze employed at Sèvres consists of a mixture of felspar and quartz. It is transparent, and rather more fusible than the body of the ware, but becomes thoroughly incorporated with it, and from its similarity in composition it expands and contracts by heat uniformly with the paste which it covers; hence it is not liable to crack and split in all directions in the manner which is so commonly observed in the glaze of the more ordinary kinds of earthenware.

The china of Berlin and Meissen is very similar in composition to that of Sèvres: these constitute what is termed hard, or true, porcelain.

English porcelain contains, in addition to the Cornish clay and felspar or flint, a large proportion of burnt bones; the glaze, which is transparent, usually contains both borax and oxide of lead to increase its fusibility. English porcelain is softer than the Chinese, French, or German porcelain, and constitutes one variety of what the French term *porcelain tendre*, the manufacture of which in France is now rarely practised.

2.—*Stoneware* is a species of porcelain in which the body of the ware is more or less coloured, less care being taken with regard to the purity of the material. It generally contains more oxide of iron, and consequently is somewhat more fusible than the best porcelain, and is usually salt-glazed in a manner shortly to be described. *Wedgwood-ware* is a fine description of stoneware.

3.—*Fine Earthenware.*—Articles of this description are very extensively manufactured in the Staffordshire Potteries, and constitute the ordinary table service of this country. The Devonshire and Dorsetshire clays are those chiefly made use of; they are mixed with a large proportion of ground flints, and yield an infusible paste which burns nearly white. The body of the ware is

not fused in the firing, but it is rendered impervious to liquids by means of a fusible lead glaze.

4.—*Common Earthenware* is made of an inferior and more fusible description of clay: both this kind of ware and the foregoing one crack easily on the sudden application of heat.

5.—The coarsest description of clay goods are bricks, tiles, flowerpots, and similar articles.

6.—Articles which are required to stand a high temperature, such as fire-bricks for lining furnaces, muffles, pots for the fusion of glass, crucibles for melting steel, and the Hessian crucibles so largely in demand in the laboratory, are made of a pure, infusible siliceous clay, the shrinking of which during drying is diminished by the addition either of burnt clay of the same description, or of, what amounts to the same thing, broken pots of the same material, which are reduced to a fine powder and incorporated with the paste. Good fire-ware is nearly white: if coloured, the presence of oxide of iron would be indicated, and this would render it fusible.

The following table gives the composition of some of the more important varieties of china and pottery ware:—

	Porcelain.					Wedgwood ware.	Lambeth stone ware.	Hessian crucible.
	Chinese.	Berlin.	English.	Sèvres.	Meissen.			
	C. Cowper	Wilson.	Cowper.	Laurent.	Laurent.	Salvetat.	Salvetat.	Berthier.
Silica	71·04	71·34	40·60	58·0	57·7	66·49	74·00	71
Alumina	...	23·76	24·15	34·5	36·0	26·00	22·04	25
Oxide of	22·46							
iron	...	1·74	...	...	0·8	6·12	2·00	4
Lime	3·82	0·57	14·22	4·5	0·3	1·04	0·60	
Alkali	2·68	2·00	5·28	3·0	5·2	0·20	1·06	
Magnesia	...	0·20	0·43	...	trace	0·15	0·17	
Bone earth and oxide of iron	...	...	15·32					
	100·00	99·61	100·00	100·0	100·0	100·00	99·87	100·0

(573) For the finer kinds of porcelain much care is taken to ensure the purity and minute subdivision of the constituents, as well as their intimate admixture. The clay is first ground between horizontal stones under water; it is next levigated in water, to allow the coarser particles to subside while the lighter ones remain in suspension. The finer suspended particles are then formed into a mixture of the consistence of thin cream; a wine pint of this being made to weigh 24 or 26 ounces: in this state the cream or pulp is mixed with the ground felspar, flint, or other material. Suppose, for example, that the pulp is to be mixed with ground flints; the flints are heated to redness, suddenly quenched in cold water, and then reduced by stamping and grinding them under water to

an impalpable powder; this also is suspended in water, a wine pint of the mixture being made to weigh 32 ounces. The two ingredients are easily mixed in the necessary proportions by taking a given measure of each pulp and thoroughly incorporating them. The mixture thus obtained is technically termed *slip*. The slip is well agitated and allowed to subside; the deposit is drained (carefully mixing it from time to time), and dried, until it has acquired sufficient consistence to allow of its being wrought by the potter. Much labour is afterwards bestowed in working this clay in such a manner as to render it of uniform composition throughout, and to preserve it free from air-bubbles. It is generally considered that the mixture is greatly improved in quality by being allowed to remain for some months before it is worked up, the mass being occasionally turned over and beaten. During this process of ripening the mass undergoes a slow change, in the course of which traces of organic matter which it contains gradually become oxidized, reducing the sulphates to sulphides, in consequence of which it evolves a slight odour of sulphuretted hydrogen, and the colour of the paste becomes somewhat darker from the formation of traces of sulphide of iron. It is of great importance in the finer specimens of ware to avoid the presence of organic matter: a single hair might spoil a delicate work of art by the disengagement of gas, and the formation of bubbles in the interior of the mass when heated.

Less labour is expended upon the coarser kinds of pottery. After the raw clay, brought from Devonshire or Dorsetshire in blocks of about 30 pounds weight, has been dried, it is ground and mixed with a certain proportion of ground flints; it is then tempered with water into a stiff paste, and passed between rollers to complete the process of fitting it for the wheel.

The mechanical operations are of the same nature in every case; and, for fashioning the clay, the *potter's wheel* is in general use. This consists of a circular slab, which can be made to revolve in a horizontal plane, either by a treddle or by a winch turned by a boy or girl. A mass of clay of the size required is dashed upon the moistened slab, and is worked by the hands, the wheel revolving during the whole time, so that the operation is a compound of moulding and turning; the article is finally trimmed up with a wooden tool, and the work is detached from the wheel by passing a wire between the slab and the vessel. The moulded articles are then allowed to dry for a day or two in a room heated from 90° to 100° F., in order to give them firmness sufficient to permit them, when necessary, to be carefully turned

on a lathe. After this operation has been completed, the handles and ornaments may be attached; these are made in moulds, and adhere readily by means of slip when pressed against the moulded mass, which is still moist. The articles have at this stage received the form which they are intended to retain, and are next subjected to heat in the *biscuit* furnace. It is necessary that the temperature be at first very gradually and carefully raised, lest the aqueous vapour, being extricated too suddenly, should deface the vessel or injure its texture. By this first firing the different articles acquire a greater degree of firmness, and can be handled without danger of breakage, but they are in a very porous state, technically termed *biscuit*. The ware in this stage readily absorbs any solution that may be placed upon its surface, and this is the period chosen for printing the patterns or designs which the finished goods are to exhibit. The colouring matter generally consists of some metallic oxide ground up with oil of turpentine or with boiled linseed oil. Blue is usually given by oxide of cobalt; green by oxide of chromium; brown by a mixture of oxides of iron and manganese; black, by the black oxide of uranium; and a pink, which is much esteemed, by a combination of oxide of tin, lime, and a minute quantity of oxide of chromium. In order to apply the colouring material, it is printed from copper plates on a thin unsized paper made for the purpose; this paper, while the colour is still moist, is applied to the surface of the biscuit; the design is soon absorbed by the ware, and the paper is washed off. The ware is now subjected to another baking or firing, for the purpose of fixing the colour and burning off the oil. For decorating the finer kinds of porcelain the metallic colour is mixed with a fusible glaze containing quartz, boracic acid, and oxide of lead, and melted. The coloured glass thus obtained is then reduced by levigation to a fine powder, and ground up with some volatile oil, in which form it is laid on in the desired pattern by means of a hair pencil. After the glazing has been completed, it is fired at a moderate heat in a muffle. In the finer kinds of decoration, the application of the colouring matter requires the nicest management. For details upon this point (and indeed upon most others connected with the art of Pottery), the reader is referred to Brongniart's great work *Sur les Arts Ceramiques*. After the application of the colouring material, the ware still remains far too porous for use, and it further undergoes the process of glazing.

The glaze for fine porcelain is prepared by levigating quartz and felspar with water, so as to form a mixture of the consistence of cream; to this a little vinegar is added, to favour the suspension

of the finely divided particles. Each article is then dipped separately into the mixture. The porous mass quickly absorbs the moisture, leaving a thin uniform film of glaze upon the surface. The goods thus prepared are then enclosed in vessels made of fire-clay, termed *seggars*, and are exposed to the most intense heat attainable in the porcelain furnace.

In glazing ordinary earthenware a similar process is adopted, but the temperature of firing is below that required in the biscuit furnace. The glaze usually consists of a fusible material containing a considerable quantity of oxide of lead; a mixture of felspar, flint, flint glass, and white lead, is in common use.

The glazing of stone-ware depends upon a peculiar mode of decomposition of common salt. Chloride of sodium is not decomposed by heat alone, and if heated with dry silicic acid no decomposition occurs; but in the presence of silica and some substance capable of imparting oxygen to the sodium, and at the same time of removing the chlorine with which it is united,—such, for instance, as steam, or oxide of iron—the salt is susceptible of decomposition at an elevated temperature; silicate of soda and hydrochloric acid, or silicate of soda and perchloride of iron, as the case may be, being formed. The various utensils, having been dipped into sand and water, are placed in the kiln, and are gradually raised to an intense heat. A certain quantity of moist salt is then thrown in: the chloride of sodium is quickly converted into vapour, and the salt is decomposed by the silica, and the oxide of iron in the clay, aided by the steam produced in the combustion of the fuel in the furnace. The perchloride of iron and hydrochloric acid pass off in vapour with the excess of salt employed, whilst the silicate of soda fuses upon the ware, and renders it impervious to liquids. The reactions may be thus represented:—

$$HO + NaCl + SiO_2 = HCl + NaO,SiO_2;\ \text{and}$$
$$Fe_2O_3 + 3\ NaCl + 3\ SiO_2 = Fe_2Cl_3 + 3\ (NaO,SiO_2).$$

It is worthy of remark, that although clay contracts very evenly by heat when its density is uniform throughout, yet if its density be unequal in different parts, the contraction is also unequal; hence though a vessel may issue smooth and well finished from the workman's hands, it often assumes a striated and uneven appearance during the process of firing; and if a stamp be impressed upon clay while soft, and the whole surface be shaved away until no further impression is visible, the mark of the stamp, after baking, reappears in a manner more or less distinct.

(574) *Ultramarine.*—Alumina enters into the formation of the pigment ultramarine, so highly prized for the purity and delicacy of its blue colour. This valuable colouring material was formerly obtained exclusively from the lapis lazuli by a tedious process, which consisted in gently calcining the stone, broken into fragments of the size of hazel-nuts; the heated fragments were then quenched in vinegar, by which they were rendered more friable, and were deprived of adhering carbonate of lime: they were next subjected to a patient levigation with a thin syrup of honey and dragon's-blood; were then made into a paste with a resinous cement; and after allowing this to remain undisturbed for some days, the ultramarine was extracted from it by suspension in hot water and subsidence. Ultramarine is now, however, manufactured artificially upon a large scale. The following process answers well upon the small scale:—100 parts of finely washed kaolin, 100 of carbonate of soda, 60 of sulphur, and 12 of charcoal, are intimately mixed, and exposed in a covered crucible to a bright red heat for three hours and a half. The residue, which should not be in a fused condition, is of a green colour. It must be well washed, dried, and mixed with a fifth of its weight of sulphur, and exposed in a thin layer to a gentle heat, little above that required to burn off the sulphur. When the sulphur has all been burned off, a fresh quantity of sulphur must be added, and the roasting repeated; and this roasting, with fresh additions of sulphur, must be repeated two or three times until the mass acquires a bright blue colour.

Considerable doubt still exists as to the true nature of the colouring matter of ultramarine. According to the experiments of Wilkens,—who has made careful analyses of a variety of samples of the artificial product, both from his own manufactory and from other sources—ultramarine is composed of two portions, one of which is constant in composition; and which he regards as the essential colouring body; it is attacked with facility by hydrochloric acid, evolving sulphuretted hydrogen: the other portion is not soluble in the acid, and contains a variable amount of sand, clay, oxide of iron, and sulphuric acid. His analyses of the pure blue pigment correspond nearly with the formula ($2\ Al_2O_3, 3\ SiO_2 + Al_2O_3, 4\ SiO_2 + NaO, S_2O_2 + 3\ NaS$), which would contain in 100 parts:—

	By calculation.	By experiment.		
SiO_2	= 37·6	40·25	39·39	40·19
Al_2O_3	= 27·4	26·62	26·40	25·85
S	= 14·2	13·42	12·69	13·27
NaO	= 20·0	19·89	21·52	20·69

and he regards the blue colouring principle as a compound of

hyposulphite of soda and sulphide of sodium. He states that the presence of iron is found not to be essential to the production of the colour; but this is still a matter of doubt. According to Brunner, a corresponding compound, in which sulphide of potassium is substituted for sulphide of sodium, is colourless.

Ultramarine, if heated in the air, gradually assumes a dull green hue; when heated with sulphur, it is not changed; if melted with borax, sulphur and carbonic acid escape, and a colourless glass remains. Sulphuric, nitric, and hydrochloric acids decompose it, and the colour is quickly destroyed. Chlorine acts still more rapidly, dissolving everything but the silica, and completely discharging the colour.

(575) CHARACTERS OF THE COMPOUNDS OF ALUMINUM.—The ordinary salts of aluminum, with the exception of the chloride, are colourless. They have a sweetish, strongly astringent taste and an acid reaction upon litmus.

Before the blowpipe the compounds of aluminum are distinguished by the formation of a pale azure blue if moistened with nitrate of cobalt and gently ignited.

In solution, they give with *hydrosulphate of ammonia* a white precipitate of hydrate of alumina, with evolution of sulphuretted hydrogen. *Ammonia* produces a bulky, semi-transparent, gelatinous precipitate of hydrate of alumina; it is nearly insoluble in excess of ammonia, or of its carbonate. *Potash* dissolves it readily; and it is reprecipitated on adding muriate of ammonia in excess. The *carbonates of the alkalies* produce the same precipitate under disengagement of carbonic acid gas, but, according to Muspratt, it retains a portion of carbonic acid. *Sulphate of potash* and sulphuric acid in slight excess added to solutions of the salts of aluminum, and evaporated, furnish well-marked octohedral crystals of alum.

Estimation of Alumina.—The quantity of alumina in the course of an analysis is always estimated from the precipitate by ammonia, or its carbonate or hydrosulphate; when thoroughly washed (an operation which, from its gelatinous nature, is tedious), and then ignited, it consists of the pure earth only.

(576) *Separation of Alumina from the Alkalies and Alkaline Earths.*—Supposing magnesia to be present in the liquid, a solution of chloride of ammonium is first added to it, unless it be powerfully acid; on the addition of caustic ammonia in slight excess, pure hydrate of alumina is precipitated. Hydrosulphate

of ammonia is a still better precipitant, if the liquid has been first nearly neutralized by ammonia; the precipitate is extremely voluminous, and requires persevering washing. On ignition it yields pure alumina. The alkalies and alkaline earths remain in the solution which has been filtered from the alumina, and their amount may be determined by the methods already detailed, (555 *et seq.*).

§ II. Glucinum (Gl=4·7). *Sp. Gr.* 2·1.

(577) Glucinum, the *beryllium* of German writers, is extracted from the emerald, or the beryl, which consist chiefly of silicate of alumina and glucina [3 (GlO, SiO_2) + Al_2O_3, 3 SiO_2]. The metal is procured from its chloride in the same way as aluminum.

Glucinum, according to the experiments of Debray (*Ann. de Chimie*, III. xliv. 5), is a white, malleable metal, fusible below the melting point of silver. It does not burn in air, oxygen, or the vapour of sulphur, but it combines readily with chlorine and iodine, and also with silicon. The vapour of water is not decomposed by it, even when the metal is heated to full redness and exposed to it. Glucinum is easily dissolved by diluted hydrochloric and sulphuric acids: nitric acid, whether diluted or concentrated, acts but feebly upon it. It is, however, readily dissolved by a solution of potash, with evolution of hydrogen, but is not acted upon by ammonia. Glucinum forms but one oxide; there is some doubt whether this should be regarded as a protoxide, or as a sesquioxide. Berzelius adopted the latter view, but later researches favour the supposition that it is a protoxide.

(578) Glucina (GlO=12·7; *Sp. Gr.* 2·967) is extracted from the beryl, of which it constitutes 13·6 per cent.: the mineral is reduced to a very fine powder, fused with carbonate of potash, treated with hydrochloric acid, evaporated to dryness, again moistened with acid and treated with water; in this way everything except the silica is dissolved: the filtered liquid is mixed with an excess of a solution of ammonia, which occasions a voluminous precipitate containing both alumina and glucina; this precipitate is well washed, and the glucina is dissolved out from the alumina by digesting the mass in a solution of carbonate of ammonia. It is again filtered, and upon boiling the clear liquid, carbonate of glucina is deposited as a white powder, which, when ignited, leaves pure glucina. Freshly precipitated glucina forms with water a somewhat tenacious mass, but it does not harden like alumina when ignited. The fixed alkalies and their carbonates dissolve it

readily. Hydrate of glucina yields a bulky, white, gelatinous mass, which absorbs carbonic acid from the air. When heated with solutions of the salts of ammonia it displaces the ammonia, and is gradually dissolved. The *chloride* ($GlCl = 40{\cdot}2$) is prepared in the same way as the chloride of aluminum; it sublimes in white, brilliant, fusible needles, which are very deliquescent; a hydrated chloride may be obtained in crystals. Glucina combines with sulphuric acid in several proportions: one of these sulphates ($GlO,SO_3 + 4\,Aq$) crystallizes in octohedra; the other sulphates are amorphous sub-salts. An *aluminate of glucina* coloured with peroxide of iron occurs native in the gem *chrysoberyl* (GlO, Al_2O_3).

(579) CHARACTERS OF THE SALTS OF GLUCINUM.—The salts of glucinum have a sweet taste (whence the name glucinum was derived, from γλυκὺς, 'sweet'), with a slight astringency, and have an acid reaction upon litmus. They are colourless, and are distinguished from those of aluminum by not yielding an alum with sulphate of potash; nor a blue when heated before the blowpipe with nitrate of cobalt; and by giving with *carbonate of ammonia* a white precipitate of carbonate of glucina, easily soluble in excess of the alkaline salt. *Ferrocyanide of potassium* gives no precipitate in their solutions: a white precipitate of hydrate of glucina is produced by *sulphide of potassium*, with extrication of sulphuretted hydrogen. If a hot solution of *fluoride of potassium* in excess be added to a hot solution of a glucina salt, scales of a sparingly soluble double fluoride of glucinum and potassium are formed.

Glucina is always estimated in the form of the anhydrous earth.

§ III. ZIRCONIUM ($Zr = 33{\cdot}6$).

(580) ZIRCONIUM is the metallic base of an earth contained in the zircon and the hyacinth, which are silicates of zirconia. The metal is procured by heating the fluoride of potassium and zirconium with potassium, and treating the residue when cold with diluted hydrochloric acid, by which everything except the zirconium is dissolved; the metal is left in a pulverulent form, and must be washed, first with a solution of chloride of ammonium, and then with alcohol; if water be used for the washing, the finely divided zirconium passes through the filter in suspension in the water. As thus obtained it is in the form of a black powder, which does not conduct a feeble voltaic current; under the burnisher it assumes a slightly metallic lustre. It has not been fused: when heated

in the air or in oxygen it takes fire below redness and burns brilliantly, forming zirconia of snowy whiteness: diluted sulphuric and hydrochloric acids do not act on it. Hydrofluoric acid dissolves it with extrication of hydrogen, forming a fluoride closely resembling fluotitanic acid; it yields a number of fluozirconates with the fluorides of the basylous metals. Boiling water gradually oxidizes zirconium; if heated with sulphur *in vacuo* it forms a brown pulverulent *sulphide* which is not decomposed by sulphuric or hydrochloric acids, and is but slowly attacked by aqua regia.

(581) ZIRCONIA ($Zr_2O_3=91$); *Sp. Gr.* 4·3.—Zirconium forms but one oxide, which Berzelius regarded as the sesquioxide, though some chemists, including Dumas and Marignac, consider it to be a binoxide, like silica, in which case its combining number would be 22·4. It may be obtained by fusing very finely powdered zircon with hydrate of potash or of soda, and saturating with hydrochloric acid. The excess of acid and moisture is expelled by evaporating nearly to dryness; on the addition of water, the chloride of zirconium is dissolved, leaving the silica: the solution is decomposed by excess of ammonia: hydrate of zirconia is thus precipitated, and is washed and ignited. Upon applying heat, it glows brilliantly just before ignition, and becomes much denser. Zirconia forms a white infusible powder, which, after ignition, is insoluble in acids, with the exception of strong sulphuric acid. The hydrate is a gelatinous, bulky, white precipitate, very sparingly soluble in carbonate of ammonia. It is insoluble in the caustic alkalies. If the salts of zirconia be precipitated by an alkaline carbonate, the precipitate becomes redissolved if agitated with excess of the alkali; a bicarbonate takes up still more, and by boiling the solution a portion of the earth is deposited. If a solution of sulphate of zirconia to which sulphate of potash has been added be boiled, a characteristic decomposition occurs, and the subsulphate of zirconia falls, whilst bisulphate of potash is formed and remains dissolved. The *chloride of zirconium* ($Zr_2Cl_3=273·7$; *Sp. Gr. of vapour*, 8·15)* crystallizes in needles: it is soluble in water and in alcohol; the crystals effloresce in the air, and lose water and hydrochloric acid, leaving an oxychloride, which is soluble.

* Two volumes of this vapour correspond to the formula $ZrCl_2=93·4$; and this strengthens the view of Marignac, according to whom zirconium is more allied to titanium than to any other element, as is particularly seen in the properties of the fluoride of zirconium, and of the fluozirconates; the latter have the general formula, MF,ZrF_2, if the atomic weight of zirconium, *Zr*, be taken as 22·4.

Zirconia is distinguished from alumina and glucina by its insolubility in the *caustic alkalies*. Its salts have a purely astringent taste; when boiled with the *sulphate of potash*, a sparingly soluble subsulphate of the earth is formed. *Tincture of galls* gives a yellow precipitate in their solutions; *ferrocyanide of potassium* does not produce a precipitate with them.

Svanberg regards zirconia not as a pure earth, but as a mixture of three. To one of the metals which he considers that he has isolated, this chemist gave the name of *Norium*; but these results at present need confirmation.

§ IV. Thorinum, Yttrium, Erbium, Terbium.

(582) Thorinum (Th=39·5) was discovered in 1829, by Berzelius, in a rare black mineral termed *thorite*, found in a syenitic rock in Norway. This metal, like aluminum, is procured from its chloride, which is a volatile compound obtained by heating an intimate mixture of thorina and finely divided charcoal in a current of dry chlorine. Thorinum much resembles aluminum, but takes fire considerably below redness, and burns with great brilliancy; the resulting oxide shows no traces of fusion. *Thorina* is considered to be a protoxide, and is remarkable for its high specific gravity (9·402). It is insoluble in solutions of the caustic alkalies, but is dissolved without difficulty in those of their carbonates. After it has been ignited it is no longer soluble in any acid except the concentrated sulphuric. Its salts have an astringent taste, and their solutions give a white precipitate with ferrocyanide of potassium. Sulphate of thorina forms with sulphate of potash a double sulphate of potash and thorina, which is soluble in water, but is precipitated by a saturated solution of sulphate of potash. The sulphate of thorina exhibits the characteristic peculiarity of being precipitated by boiling its solution, but it is redissolved slowly on cooling. Its crystals, like those of sulphate of yttria, when heated, become milk-white without altering in form. Oxalic acid gives with salts of thorina, even in acid solutions, a white insoluble oxalate of the earth.

(583) Yttrium is obtained by a method similar to that employed for aluminum and glucinum. This metal is not oxidized when heated to redness either in air or in aqueous vapour; in oxygen it burns with superb scintillations; dilute acids and alkalies dissolve it slowly.

Yttria is a very rare earth, found in *gadolinite*, which is a sili-

cate of yttria, glucina, cerium, and iron; it occurs also in *yttrotantalite* combined with tantalum, and in one or two other very rare minerals. It is considered to be a protoxide, and forms a white earthy powder of sp. gr. 4·842; it is insoluble in the caustic alkalies, but the carbonates of the alkalies, especially that of ammonia, dissolve it.

Its salts are colourless, they have a sweetish astringent taste; their solutions yield a white precipitate with ferrocyanide of potassium. Its most characteristic salt is the sulphate, the crystals of which lose water at 176°, and become milk white, without change of form; on being put into water they do not resume their transparency.

Mosander states that three bases have been confounded under the name of yttria; to the more abundant of these he gives the name of yttria: the other two he distinguishes as *erbia* and *terbia*. The oxide of erbium has a yellowish tint, but its salts are colourless; the salts of terbium have a pale rose colour.

§ V. Cerium, Lanthanum, and Didymium.

(584) Closely allied to the metals of the earths are three other metals, the oxides of which, being more or less coloured, have not generally been considered as belonging to the earths proper. They need no lengthened description, as they have hitherto been found only in a few rare minerals, of which *cerite*, a hydrated subsilicate of cerium, is the most common. Till recently they were all confounded together under the name cerium.

Cerium appears to form two oxides—a protoxide, and a sesquioxide, both of which yield salts with acids. The best known of these is the double sulphate of protoxide of cerium and potash, which is insoluble in sulphate of potash. The sesquioxide has a yellowish tinge, and its salts are yellow or red.

Lanthanum (so named from λανθάνω, 'to lie hid') was discovered by Mosander, in 1841. It forms only one oxide, which is buff-coloured, and freely soluble in diluted nitric acid. It forms colourless, astringent salts, which give a white precipitate with the soluble oxalates.

Didymium also furnishes but a single oxide, which is of a dark-brown colour, when anhydrous; in the hydrated state it absorbs carbonic acid from the air. Its salts are pink or violet-coloured, and are not precipitated at ordinary temperatures by sulphide of ammonium.

CHAPTER XIV.

GROUP IV.—METALS MORE OR LESS ALLIED TO IRON.

§ I. ZINC ($Zn=32{\cdot}7$). *Sp. Gr.* 6·8 to 7·1; *Boiling Pt.* 1904° F.

(585) ZINC, or *spelter*, as it is often called in commerce, has been known in the metallic form since the time of Paracelsus. Its ores occur in considerable abundance, though it is never met with in the native state. Much of the zinc of commerce is supplied from Silesia, where the ore wrought is *calamine*; the common or rhomboidal calamine, a carbonate of zinc, is the most important variety, though the prismatic or electric calamine, a hydrated sub-silicate of zinc, is found often in the Carinthian ores: it is much more difficult of reduction. Carbonate of zinc is also extensively worked in Belgium, where it is found mixed with clay. In the Mendip Hills, in Somersetshire, the carbonate of zinc is associated with magnesian limestone. *Blende*, or sulphide of zinc, is worked in England to some extent; it usually accompanies the sulphide of lead (or galena) in the mountain limestone. In New Jersey *red oxide of zinc* has been found in large quantities both massive and crystallized; the colour is due to admixture with oxides of manganese and iron. It forms a valuable ore, and is easily reduced. In the year 1858, 11,556 tons of zinc were extracted from English mines.

(586) *Extraction of Zinc from its Ores.*—In the extraction of zinc, whether from blende or from calamine, the ore is crushed between rollers, and undergoes a process of roasting; in the case of blende a preliminary mechanical treatment is required, in order to separate the galena as completely as possible, as the presence of lead would occasion rapid destruction of the crucibles during the subsequent reduction of the metal. The roasting of blende is tedious, and requires to be carefully performed; the sulphur burns away as sulphurous acid, and the zinc becomes oxidized; $ZnS+3\,O$ yield $ZnO+SO_2$. Calamine also yields oxide of zinc when roasted, whilst the carbonic acid and water are expelled. The roasted ore from either source is mixed with half its weight of powdered coke or anthracite, and introduced into crucibles of peculiar construction. The method of reduction practised in England offers one of the few instances in which distillation, *per descensum*, is still prac-

tised :—a circular furnace, somewhat similar to that used in making glass, is employed : in this furnace six large clay crucibles, (three of which are represented in the section at A, A, A, fig. 323,) each 4 feet high and 2½ feet in diameter, are arranged, three on each side of the firebars; one of these crucibles is shown in section in the figure. In the bottom of each crucible is an opening, to which a short iron pipe is attached, which passes out through the bottom of the furnace; to this iron tube a second wider tube, *b*, about eight feet long, is fastened in such a manner as to be readily removeable; beneath the open end of this tube a sheet-iron vessel, *c*, is placed to receive the zinc. The bottom of the crucible is then loosely plugged with large pieces of coke, and a charge containing from 4 to 5 cwt. of the mixture of calcined ore and coal is introduced into each pot, and the cover is carefully luted on. Carbonic oxide is first evolved abundantly, and burns with a blue flame at the mouth of the short iron tube; in a few hours the colour of the flame changes to brown, when the cadmium, which is more volatile than zinc, comes over, and may be condensed. When the colour of the flame changes to bluish-white the zinc is distilling nearly pure. The flame is then extinguished by attaching the longer tube, and the metal, which is condensed partly in powder, partly in stalactitic masses, falls down into the iron vessels, *c*, *c*, placed for its reception. The zinc, being volatile at very high temperatures, boils and distils as the operation proceeds. In order to prevent the pipe, *b*, from becoming choked, it is occasionally removed, and the zinc detached from it. The crude metal is mingled with a good deal of oxide; it is therefore

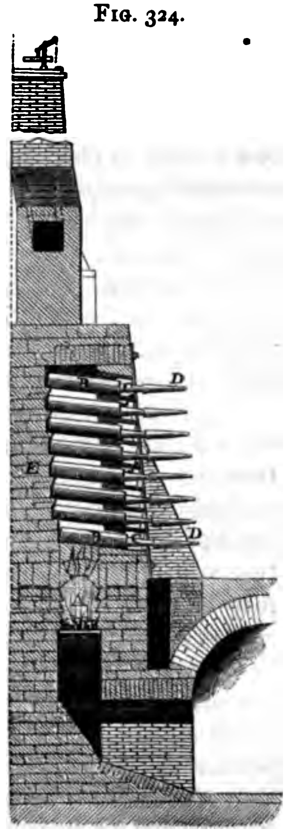
FIG. 323.

re-melted, skimmed, and cast into ingots; or (if intended for rolling) into sheets, and then laminated at a temperature of about 250°. Calamine, which contains 52 per cent. of metal, does not yield on an average above 30; the greater part of the silicate of zinc, which calamine almost always contains, escaping decomposition.

(587) In Silesia the distillation is effected in muffle-shaped earthen retorts, which are ranged in two rows on the same plane in a long furnace, back to back: the outer end of each retort is provided with two apertures; the lower one is employed for introducing the charge, and is afterwards carefully luted up, whilst the upper one is for receiving a bent earthen pipe which carries off the metal as it distils.

(588) In Belgium the distillation is managed quite differently. The ores treated in that country are of two kinds, both occurring in a matrix of clay above a bed of dolomite: one is a red variety, containing about 33 per cent. of zinc, with a good deal of oxide of iron, but admitting of reduction at a moderate temperature; the other is a white ore, also a calamine, which contains about 46 per cent. of zinc, and requires a much higher temperature for its reduction. These two species of ore are kept distinct from each other during the process of smelting. The calamine, having been washed to remove the clay, is roasted, during which operation it loses about 25 per cent. of water and carbonic acid. After this it is reduced to a fine powder, and thoroughly mixed with half its weight of coal-dust: this mixture is then introduced into clay retorts about three feet eight inches long and six inches in diameter; each retort is charged with about 40 lb. of the mixture of coal and roasted ore. Forty-two of these retorts are arranged in an arched furnace, in rows of six, placed one above another. The backs of the retorts rest on notches in the wall, E, fig. 324, and are supported on a slightly higher level than the open extremities, which rest in front upon iron plates, *f*, *f*, *f*. To

FIG. 324.



each retort an open, somewhat conical, cast-iron pipe, C, is luted; this serves as a receiver for the distilled metal, and upon each of these receivers is fitted a second receiver of sheet iron, D, with an opening at the extremity for the escape of gas. The fire by which the retorts are heated is shown at A. In such a furnace two charges may be worked off in twenty-four hours. During the operation the small adapters, D, D, are withdrawn once in two hours, and the liquid zinc which has condensed in the receivers is raked out into a large ladle and cast into ingots. When the distillation is complete, the residues in the retorts still retain nearly 25 per cent. of zinc, which is chiefly in the form of silicate of the oxide; this portion is entirely wasted (Piot and Murailhe, *Ann. des Mines*, IV. v. 165).

The retorts in the upper part of such a furnace necessarily receive less heat than those in the lower part, and hence this process is particularly well adapted to the Belgian ores, because the poorer ones, which require less heat, can be employed in charging the upper retorts.

(589) *Preparation of Pure Zinc.*—Commercial zinc contains a small quantity of lead, iron, and of a peculiar carbonaceous matter, besides occasionally traces of arsenic and of copper. The best method of obtaining the metal in a state of purity consists in transmitting sulphuretted hydrogen through a slightly acidulated solution of sulphate of zinc, filtering from any precipitate which may be formed; and after boiling the solution, in order to expel the sulphuretted hydrogen, precipitating the zinc in the form of carbonate by the addition of carbonate of soda. The carbonate, when ignited, is converted into oxide of zinc, which must be distilled in a porcelain retort with charcoal prepared from loaf sugar.

(590) *Properties.*—Zinc is a hard, bluish-white metal, which, when a mass of it is broken across, exhibits a beautiful crystalline fracture. It is rather brittle at ordinary temperatures, but between 200° and 300°, it is possessed of considerable ductility and malleability, and it may be laminated and wrought with ease: at a temperature a little higher than this, it again becomes so brittle that it may be pulverized in a mortar. It fuses at 773°, and at a bright-red heat it may be volatilized: the temperature of its boiling point is estimated by Deville at 1904° F.: if its vapour be exposed to the air, it burns with great splendour and is converted into oxide, which is deposited in copious white flocculi. Zinc soon tarnishes when exposed to a moist atmosphere, and becomes covered with a thin, closely-adhering film of oxide, by which the metal beneath is protected from further change. This property renders zinc valuable for a variety of economical and domestic purposes. It

combines, however, readily at ordinary temperatures with chlorine, bromine, and iodine, if moistened with water; it is also easily attacked by all the mineral acids, and is employed to decompose diluted sulphuric acid when hydrogen is required. A strong solution of potash also acts upon zinc if boiled upon it; hydrogen being liberated, whilst oxide of zinc is formed and dissolved in the alkaline solution; $Zn + HO,KO = H + ZnO,KO$. Zinc precipitates most of the basylous metals less oxidizable than itself in the metallic state from their solutions.

(591) *Uses.*—The uses of zinc are daily extending. From its durability, cheapness, and lightness, it is frequently employed as a substitute for lead in roofing. It is employed as the oxidizable metal in the construction of the voltaic battery. Sheet iron coated with zinc, or *galvanized* iron as it is often called, is also used for roofing; the iron gives strength, whilst the zinc protects it from oxidation, and it is not combustible like zinc alone. Galvanized iron is prepared by cleaning sheet iron thoroughly as in making tin plate (675), and plunging the metal into a bath of molten zinc, covered with sal ammoniac; the surface of the zinc is by this means kept free from oxide, which is dissolved by the sal ammoniac, and the two metals unite readily. A tougher and superior article is obtained by first coating the iron plate with a very thin film of tin by a voltaic action, and then immersing the metal into the melted zinc.

Zinc has a considerable power of dissolving iron, in consequence of which it corrodes the iron pots in which it is melted: an alloy of zinc with a small proportion of iron is formed, which is less fusible than zinc, and crystallizes in large plates on cooling.

Zinc forms several valuable alloys. Of these, brass is the most important: it consists of about 2 parts of copper to 1 of zinc. German silver is brass containing a portion of nickel, to which its white colour is due. Of late years zinc in powder has been employed as the basis of a pigment well adapted to resist the action of the weather. The oxide of zinc, under the name of *zinc white*, has also been employed as a substitute for white lead, to form the basis of a white paint; but it wants the opacity and dead whiteness for which the carbonate of lead is so much valued. Oxide of zinc has likewise been substituted for red lead with great advantage in the preparation of glass for optical purposes (499).

(592) OXIDE OF ZINC ($ZnO = 40{\cdot}7$); *Sp. Gr.* 5·612.—It is possible that the film which is formed upon the surface of metallic zinc by exposure is a suboxide; but only one well ascertained oxide of the metal is known, and this is regarded as a protoxide: this

oxide is occasionally deposited in furnace flues in yellowish six-sided prisms; but it is generally obtained in the form of a white flocculent powder. If zinc be thrown in small quantities at a time into a capacious clay crucible previously heated to whiteness, it burns with a brilliant flame and deposits large white flakes of the oxide; but when thus prepared, it is mechanically mixed with particles of the metal, from which it may be separated by levigation with water; the heavier metallic portions subside quickly and leave the oxide in suspension. The process of manufacturing this oxide when it is required as a pigment, consists in distilling zinc from clay retorts into chambers through which a current of air is maintained. The volatilized metal burns at the high temperature to which it is exposed under these circumstances, and the oxide is deposited in a series of condensing chambers. An impure oxide, sold under the name of *tutty*, is obtained from the flues of furnaces in which brass is melted.

Oxide of zinc becomes yellow when heated, but recovers its whiteness as the temperature falls. It is readily soluble in acids. The hydrated oxide (ZnO,HO) is precipitated from the solutions of the salts of zinc by the addition of potash or of soda; it is redissolved by an excess of the alkaline liquid.

(593) SULPHIDE OF ZINC: *Blende* (ZnS=48·7); *Sp. Gr.* 4·1. —This compound is one of the most abundant minerals of zinc. It contains 67·14 per cent. of the metal and 32·86 of sulphur. When pure it is of a pale brown colour, but generally it is nearly black from admixture with sulphide of iron. It sometimes occurs massive, but is usually crystallized in rhombic dodecahedra, though it occurs in other forms of the regular system. Metallic zinc does not unite readily with sulphur: but if heated rapidly in mixture with cinnabar (or sulphide of mercury), the mercury is volatilized, and sulphide of zinc is formed with almost explosive violence. Sulphide of zinc does not fuse when heated: when roasted in the air it absorbs oxygen; at a low temperature a large portion of it is converted into sulphate of zinc, but at a higher temperature sulphurous acid is formed, and oxide of zinc is left. It is only slightly attacked by sulphuric and hydrochloric acids, but nitric acid and aqua regia dissolve it readily. When the salts of zinc are mixed with hydrosulphate of ammonia, a white, gelatinous, hydrated sulphide of zinc is precipitated, which absorbs oxygen quickly from air, and is readily dissolved by acids.

(594) CHLORIDE OF ZINC (ZnCl=68·2).—This salt may be procured by heating the metal in chlorine gas, but it is generally obtained by dissolving the metal in hydrochloric acid; the acid is

decomposed, its chlorine unites with the zinc, forming chloride of zinc which is retained in solution, whilst its hydrogen escapes in the gaseous form. When this solution is heated, it loses water till the temperature rises to 480°; it then becomes anhydrous, but remains fluid, and may be heated to above 700° without emitting an inconvenient amount of fumes; hence it is sometimes employed as a hot-bath for maintaining objects at a high but measurable and regulated temperature. At a red heat it distils. Pure chloride of zinc is a white, very deliquescent substance, fusible at about 212°; it is powerfully corrosive when applied to the skin. Under the name of *Burnett's Disinfecting Fluid,* its solution has been largely used as an antiseptic, and as a preservative of wood and vegetable fibre against decay. Chloride of zinc is soluble in alcohol.

Chloride of zinc absorbs ammoniacal gas freely. It also unites with oxide of zinc in several proportions and forms a number of oxychlorides. Chloride of zinc forms double salts with the chlorides of the alkaline metals; a concentrated solution of the double chloride of zinc and ammonium ($H_4NCl+ZnCl$) is used for the purpose of removing the film of oxide from the surface of metals, such as zinc, iron, or copper, which are to be united by the operation of soldering.

(595) SULPHATE OF ZINC ($ZnO,SO_3+7\ Aq=80{\cdot}7+63$; *Sp. Gr., anhydrous,* 3·681, *cryst.,* 1·931) is obtained in large quantities as a residue in the ordinary process of procuring hydrogen by the action of diluted sulphuric acid. It may also be prepared by roasting sulphide of zinc at a low temperature, lixiviating the mass and crystallizing. It crystallizes in colourless four-sided prisms, which constitute the *white vitriol* of commerce. In a dry air it is efflorescent; it is soluble in 2½ parts of water at 60°, and melts in its water of crystallization when heated. Sulphate of zinc is used medicinally in small doses; it is likewise prepared largely for the calico printer. It forms double sulphates with potash and with ammonia, which crystallize with 6 Aq. Several subsulphates of zinc may also be obtained.

(596) CARBONATE OF ZINC ($ZnO,CO_2=62{\cdot}7$; *Sp. Gr.* 4·4) is found native, both massive, and crystallized, in forms derived from the rhombohedron. It is usually of a greyish or yellowish colour, forming one variety of *calamine,* which is so named from its property of adhering, after fusion, in the form of reeds, to the base of the furnace. It readily loses carbonic acid when ignited. Calamine contains 64·8 per cent. of oxide of zinc, and 52 per cent. of the metal. No neutral carbonate of zinc can be obtained from the salts of the

metal by double decomposition. When a hot solution of a salt of zinc is precipitated by a boiling solution of an alkaline carbonate, a hydrated oxycarbonate is formed, consisting of ($8\,ZnO,3\,CO_2 + 6\,Aq$; Schindler). Several other basic carbonates of zinc may be formed.

The other variety of calamine becomes electric by heat; it is a hydrated subsilicate ($2\,ZnO,SiO_2 + Aq$).

(597) CHARACTERS OF THE SALTS OF ZINC.—The salts of zinc are colourless; their solutions have an astringent, metallic taste, and act rapidly and powerfully as emetics.

They are distinguished by giving no precipitate in acid solutions with *sulphuretted hydrogen*; but they yield a white hydrated sulphide of zinc with *hydrosulphate of ammonia*; a white hydrated oxide with *potash, soda,* or *ammonia,* soluble in excess of the alkali; a white basic carbonate of zinc with the *carbonates of the alkalies,* soluble in carbonate of ammonia but not in the carbonates of the fixed alkalies; they also yield a white precipitate with *ferrocyanide of potassium.*

Before the blowpipe, in the reducing flame on charcoal, the metal is reduced and volatilized, burning into white fumes of oxide of zinc. If placed on charcoal and moistened with a solution of nitrate of cobalt, the compounds of zinc when heated in the oxidating flame leave a green residue, which is not fusible.

(598) *Estimation of Zinc.*—Zinc is best precipitated for analysis by carbonate of potash, the whole solution being evaporated down to dryness; the residue, which contains the carbonate of zinc, is washed with boiling water, dried, and converted by ignition into oxide of zinc, which is weighed. The oxide contains, in 100 parts, 80·39 of zinc and 19·61 of oxygen. If ammoniacal salts be present, an excess of the carbonate of potash should be used sufficient to decompose the salts of ammonia completely, the ammonia being wholly expelled as carbonate of ammonia during the process of evaporation. The foregoing process is not applicable to the separation of zinc from any but the alkaline bases.

(599) *Separation of Zinc from the Alkalies and Alkaline Earths.*—This may be effected by the addition of hydrosulphate of ammonia to the solution after it has been neutralized by ammonia; the zinc is thus precipitated as hydrated sulphide: it must be washed with a solution of sulphuretted hydrogen, to prevent its oxidation, then redissolved in hydrochloric acid, and evaporated to dryness with excess of carbonate of soda: the soluble salts must be washed from the carbonate of zinc, which is to be converted into oxide by ignition, and then weighed.

The separation of Zinc from Alumina and Glucina may be effected by dissolving all the bases by means of an excess of caustic potash, and adding hydrosulphate of ammonia: in this case sulphide of zinc is alone precipitated; it may be collected and its amount determined in the manner just described.

§ II. Cadmium (Cd=56). *Sp. Gr.* 8·6; *Boiling Pt.* 1580°; *Comb. Vol. of Vapour,* 2.

(600) Cadmium was discovered by Stromeyer, in 1818. It is occasionally found as sulphide of cadmium, accompanying the ores of zinc, and is obtained as an accidental product during the extraction of the latter metal. Being more volatile than zinc, the greater part of the cadmium sublimes among the first portions of the distilled metal, from which it may be extracted by dissolving them in sulphuric acid, and precipitating the cadmium as sulphide by means of sulphuretted hydrogen; the sulphide may be dissolved in strong hydrochloric acid, precipitated by carbonate of ammonia, and reduced in an earthen retort by ignition with charcoal; the metal distils over at a heat below redness.

Cadmium is of a white colour, resembling tin, and, like it, creaks when a rod of it is bent; it is so soft that it leaves its traces upon paper, and possesses considerable malleability and ductility. Cadmium fuses at 442°, and may be obtained in octohedral crystals as it cools. It boils at 1580°, furnishing a vapour, the combining volume of which is 2 (Deville and Troost). In the atmosphere it undergoes little change, but when thrown into a red-hot crucible it takes fire, depositing brownish-yellow fumes of oxide. It is dissolved with evolution of hydrogen when heated in sulphuric or hydrochloric acid slightly diluted; nitric acid dissolves it still more freely.

(601) Oxide of Cadmium ($CdO=64$; *Sp. Gr.* 6·93) is obtained as a brown anhydrous powder, by burning the metal in air, or by igniting the nitrate of cadmium; it is not fusible or volatile in the furnace. A white hydrated oxide of cadmium may be obtained by decomposing its salts by a fixed alkali; ammonia in excess redissolves it, but potash and soda have no such effect: even the anhydrous oxide is soluble in ammonia. Carbonate of ammonia does not dissolve oxide of cadmium either in the anhydrous or the hydrated form.

Sulphide of Cadmium ($CdS=72$) constitutes the mineral known as *Greenockite,* which occurs crystallized in six-sided prisms.

It may be formed artificially by transmitting a current of sulphuretted hydrogen through a solution of a salt of cadmium; it greatly resembles orpiment in appearance, but is distinguished from it by its want of volatility when heated, and by its insolubility in ammonia and in the sulphides of the alkaline metals. It forms a bright yellow pigment highly valued both for the purity and permanence of its tint.

CHLORIDE OF CADMIUM ($CdCl + 2\ Aq$) crystallizes easily. The *iodide* may also be obtained without difficulty in crystals, which have a pearly lustre. It is anhydrous, and fuses readily on the application of heat. This salt is easily obtained by digesting metallic cadmium in water with free iodine, and evaporating the solution; it is employed for iodizing collodion for photographic purposes (884).

(602) CHARACTERS OF THE SALTS OF CADMIUM.—The salts of cadmium are colourless, and resemble those of zinc. They may be readily distinguished by the yellow precipitate of sulphide of cadmium which they yield with *sulphuretted hydrogen* in acid solutions; this precipitate is insoluble either in ammonia or in the alkaline sulphides. *Potash and soda* give a precipitate of white hydrated oxide, insoluble in excess; *ammonia*, a similar precipitate, very soluble in excess; *carbonates of potash, soda, and ammonia*, a white carbonate, insoluble in excess; *oxalic acid*, a white precipitate, soluble in ammonia; *ferrocyanide of potassium*, a yellowish-white precipitate, soluble in hydrochloric acid.

Before the blowpipe they are decomposed, and on the cool part of the charcoal a ring of brown oxide of cadmium is deposited, due to the reduction and subsequent combustion of the metal.

Estimation of Cadmium.—Cadmium is readily separated from all the foregoing metals by the action of sulphuretted hydrogen, which causes a precipitate of the yellow sulphide of cadmium from an acidulated solution of its salts. This precipitate is redissolved in nitric acid, decomposed by an excess of carbonate of soda, evaporated to dryness, washed from the soluble salts, and the resulting carbonate of cadmium is heated to redness, by which it is converted into oxide; it is then weighed: 100 grains of oxide of cadmium contain 87·5 of the metal.

§ III. COBALT ($Co = 29{\cdot}5$). *Sp. Gr.* 8·95.

(603) COBALT appears to have been first recognised as a distinct metal by Brandt, in 1733. It generally occurs in combination with arsenic, as speiss-cobalt or tin-white cobalt ($CoAs$), but occa-

sionally it is found as cobalt glance, which is a compound of the arsenide and the sulphide of the metal ($CoS_2,CoAs$). Cobalt is never met with in the native state, except as an ingredient in meteoric iron in small proportion. The black oxide has been found to some extent in the Western States of America, mixed with the sulphide of cobalt and with variable proportions of the oxides of nickel, manganese, iron, and copper. The ores of this metal occur chiefly in the primitive rocks, and are usually very complicated; containing nickel, iron, and often bismuth and copper, mineralized either by sulphur or by arsenic, or by both together.

Extraction.—It not easy to obtain cobalt in a state of purity. On a small scale the ore may be treated as follows:—It is first roasted at a low but gradually rising temperature, in order to expel the greater portion of the arsenic; after which it is dissolved in aqua regia, and evaporated to dryness to expel the excess of acid; it is then redissolved in water, and a current of sulphuretted hydrogen is transmitted through the solution. Bismuth, copper, and the remainder of the arsenic are thus precipitated as sulphides. The filtered liquid is boiled to expel the excess of the gas, and a slight excess of nitric acid is added to the boiling liquid, to peroxidize the iron; when cold, it is diluted and supersaturated with ammonia; the peroxide of iron is precipitated, carrying with it a little cobalt, but the bulk of the cobalt remains dissolved, with any nickel which the ore may have contained.

The exact separation of cobalt from nickel is tedious. Two methods have been proposed, one by Rose, the other by Liebig (617). Rose's method is the following:—The two metals are thrown down from the ammoniacal liquid as sulphides, by the addition of hydrosulphate of ammonia. The sulphides are redissolved in nitric acid, the solution is then largely diluted, and acted upon by a current of chlorine; after this it is digested in a closed vessel for 12 hours upon powdered carbonate of baryta. The chlorine converts the cobalt into sesquioxide, which is gradually precipitated by the baryta, and remains mixed with the excess of carbonate of baryta employed. This precipitate is again dissolved in hydrochloric acid; the baryta is removed by adding sulphate of soda, and the oxide of cobalt precipitated by caustic soda: the precipitate must then be well washed with boiling water, and reduced in a current of hydrogen gas, which leaves the metal in the form of a black, highly magnetic powder. When nickel is to be separated from cobalt for purposes of analysis, T. H. Henry recommends the substitution of a solution of bromine for chlorine gas in the fore-

going process. Bromine may be used instead of chlorine in many analogous cases with great convenience.

If oxide of cobalt be reduced in a crucible lined with charcoal, a carbide of cobalt is formed, which may be obtained in a well-fused button. The crucible may be lined with charcoal for this purpose by dipping it into water, and filling it completely with charcoal finely powdered, and sufficiently moistened to render it coherent when firmly beaten into the crucible; a cylindrical cavity is then scooped out of the middle of the mass, and its interior is carefully smoothed with a glass rod, after which the crucible is allowed to dry slowly. Pure cobalt may also be procured by heating the oxalate in a covered porcelain crucible, enclosed in a second earthen one, with the cover luted down; the crucibles are then exposed for an hour to the most intense heat of a forge: a well-fused button of cobalt may generally be obtained in this manner.

Properties.—Metallic cobalt is nearly as infusible as iron. It is of a reddish-grey colour; is hard, brittle, and strongly magnetic. Deville however states that by reducing the oxalate in a crucible lined with lime, he obtained a metallic button which yielded a wire of a tenacity nearly double that of an iron wire of the same diameter. It is dissolved slowly, with evolution of hydrogen, by hydrochloric and diluted sulphuric acids, and it is freely oxidized by nitric acid; when exposed to the atmosphere, it becomes slowly converted into oxide. Cobalt is not used in the metallic state in the arts. Many of the compounds of cobalt are remarkable for the beauty and brilliancy of their colour, and are used as pigments.

The alloys of cobalt are unimportant. Its compounds with arsenic are interesting, as they supply the greater part of the cobalt employed in the arts. *Tin-white cobalt,* when pure, contains an atom of each of the two metals ($CoAs$), or 28·57 per cent. of cobalt and 71·43 of arsenic; but portions of the cobalt are frequently displaced by nickel and iron. The purest specimens of this mineral are obtained from Tunaberg; the ore from this locality is the best material to employ in preparing the compounds of cobalt. Arsenide of cobalt melts at a moderate red heat. *Bright white cobalt,* or *cobalt glance* ($CoS_2 + CoAs$), corresponds in composition to mispickel: it crystallizes in cubes, octohedra, or dodecahedra, and contains 35·92 per cent. of cobalt, 44·92 of arsenic, and 19·16 of sulphur. These minerals are violently decomposed by nitric acid or by aqua regia, and are readily attacked when heated in a current of gaseous chlorine. They are also decomposed when roasted in a current of air.

(604) Oxides of Cobalt.—There are two well-marked oxides

of cobalt, the protoxide, CoO, which is the salifiable base of the metal, and the sesquioxide, Co_2O_3; these two oxides are capable of uniting with each other in different proportions. According to Schwarzenberg an acid oxide, Co_3O_5, may be obtained in combination, by strongly igniting the protoxide or the carbonate with hydrate of potash, in which case a crystalline compound is formed, which when dried at 212°, consists of KO, 3 Co_3O_5 + 3 Aq.

Protoxide (CoO = 37·5)—This oxide is of an ash-grey colour; when heated in the air it absorbs oxygen, and becomes black. It is soluble in acids, and forms solutions which, when concentrated, are of a beautiful blue colour, but they become pink on dilution. The oxide forms an important article of commerce, from its employment for the production of a blue colour in painting on porcelain. When describing the preparation of nickel, a process will be detailed which furnishes the oxide of cobalt fit for this purpose (612). Protoxide of cobalt combines with bases as well as with acids. If fused with hydrate of potash it forms a blue compound; when heated with nitrate of magnesia, a pale pink residue, formed by the combination of the magnesia with oxide of cobalt, is obtained; with alumina it forms the blue pigment known as Thénard's blue, and with oxide of zinc the compound constitutes Rinman's green.

The *zaffre* of commerce is a very impure oxide of cobalt, procured by imperfectly roasting cobalt ore, mingled with 2 or 3 times its weight of siliceous sand.

Smalt is a beautiful blue glass coloured by oxide of cobalt; it is chiefly manufactured in Saxony. In preparing smalt, the cobalt ore is first roasted; but the roasting is arrested at a particular stage, the object being to oxidize the cobalt, whilst the nickel, copper, and iron remain in combination with arsenic and sulphur; it is necessary to leave a sufficient amount of arsenic in the mass to retain these metals, as the admixture of a very small quantity of the oxides either of iron, nickel, or copper with the glass, seriously injures the purity of its colour. From 4 to 5 parts of the roasted ore in powder are next mingled with 10 parts of ground calcined quartz and 4 parts of carbonate of potash, and the mixture is slowly melted in pots arranged in a furnace resembling that used in making ordinary glass. The oxide of cobalt combines with the fused silicate of potash; a deep blue glass is thus formed, whilst the mixed arsenides and sulphides of nickel, copper, and iron fuse, and collect at the bottom of the pot, in the form of a brittle mass, of metallic appearance, commonly known as *speiss*. The pot is then skimmed, and the glass is ladled out, and poured into cold water,

by which means it is split into innumerable fragments: the speiss is cast into ingots and used in the manufacture of nickel. The broken glass is stamped to powder, and subsequently ground between granite stones, which are caused to revolve under water, in a vessel through which a gentle stream of water is continually flowing. The water as it flows off carries with it the powdered smalt in suspension: it is made to pass through a number of depositing vessels, so arranged that the overflow from the first shall pass into the second, that from the second into the third, and so on: each of these vessels is successively larger than the one which precedes it, so that the period for which the washings are retained in each goes on progressively increasing, and the particles deposited progressively increase in the minuteness of their subdivision; the colour becoming less intense, the greater the degree of subdivision of its particles. Smalt is used largely by paper-stainers, to produce a blue colour, and it is employed to some extent by laundresses, for correcting the yellow tinge in linen.

Another valuable pigment into the composition of which cobalt enters is of a pale blue colour, and is known as *Thénard's blue*. The most approved method of preparing it consists in precipitating nitrate of cobalt by means of phosphate of potash, and mixing the precipitate whilst still moist with four or five times its bulk of the gelatinous mass obtained by adding carbonate of soda to a dilute solution of alum perfectly free from iron. The mixture is dried and then exposed to a dull red heat in a covered crucible. The brilliancy of the colour is much impaired by the reducing action of the combustible gases of the fuel. The best preventive of this effect is found to consist in placing a little red oxide of mercury at the bottom of each crucible; by the decomposition of this oxide an atmosphere of oxygen is obtained, and the metallic mercury is dissipated in vapour (Regnault, *Cours Elém.*, vol. iii. p. 150).

Rinman's green is a pigment of analogous composition, containing oxide of cobalt combined with oxide of zinc.

Hydrated oxide of cobalt (CoO, HO) is precipitated by the addition of potash or of soda to solutions of any of its salts. The pale blue precipitate which is first formed is a subsalt of cobalt, but if an excess of alkali be used, it quickly becomes violet, and finally rose-coloured, which is the true colour of the hydrated oxide: these changes occur most rapidly if the liquid be warmed. It becomes of a dingy green if exposed while moist to the air, owing to the gradual absorption of oxygen. The hydrated protoxide is readily dissolved by solution of carbonate of ammonia, and also by excess

of ammonia, especially in the presence of a neutral salt of ammonia.

Sesquioxide of Cobalt ($Co_2O_3=83$) may be prepared by suspending the hydrated protoxide of the metal in water, and transmitting a current of chlorine through the liquid; chloride of cobalt is formed and dissolved, whilst a black hydrated sesquioxide of cobalt is precipitated, Co_2O_3, 3 HO. The reaction may be thus expressed: $3\ (CoO,HO)+Cl=Co_2O_3,3\ HO+CoCl$. If the oxide of cobalt be suspended in a solution of potash instead of in pure water, the whole of the cobalt is precipitated as sesquioxide. It may be rendered anhydrous by a careful application of heat, but if strongly heated it becomes converted into a black oxide (CoO, Co_2O_3), corresponding with the magnetic oxide of iron. This magnetic oxide is sometimes deposited in small hard, anhydrous, brilliant, steel-grey octohedra when a pure aqueous solution of chloride of roseocobaltia (605) is boiled. In this form it is insoluble in nitric acid, in hydrochloric acid, and in aqua regia: it is but slowly attacked by heating it with oil of vitriol or with bisulphate of potash. The basic powers of the sesquioxide are extremely feeble. Cold sulphuric, nitric, hydrochloric, phosphoric, and acetic acids dissolve the hydrated oxide, but the salts are gradually converted at ordinary temperatnres into those of the protoxide, and this change is immediately effected if the solutions are heated.

(605) AMMONIACAL COMPOUNDS OF COBALT.—When a solution of a salt of cobalt in ammonia is exposed to the air, it absorbs oxygen rapidly, although the hydrated protoxide of cobalt alone exhibits this tendency to a small extent only. If the hydrated oxide be dissolved in a solution of chloride of ammonium containing free ammonia, the absorption of oxygen proceeds quickly, and a remarkable violet-red colour gradually developes itself in the liquid. If at this stage the liquid be supersaturated with hydrochloric acid in the cold, a heavy brick-red crystalline powder is precipitated, the chloride of *roseocobaltia* (Co_2Cl_3, 5 H_3N, 2 HO, Genth and Gibbs). And this compound, if boiled, is converted into a purple precipitate of chloride of *purpureocobaltia* (Co_2Cl_3 5 H_3N, Genth and Gibbs), which separates in crystals, leaving the solution nearly colourless: this precipitate may be dissolved by heating it in water slightly acidulated with hydrochloric acid, and as the liquid cools, beautiful ruby-red octohedral crystals are formed (F. Claudet). This remarkable compound is quite insoluble in boiling hydrochloric acid, and may be employed as a means of obtaining chemically pure cobalt: at a red heat it loses ammonia and hydrochlorate of ammonia, leaving chloride of cobalt. The latter

may be reduced to the metallic state by passing a current of hydrogen gas over it in a tube heated to redness. When digested with water upon oxide of silver, the chlorine is withdrawn from the new compound, whilst the oxygen of the oxide takes its place; a red strongly alkaline liquid, oxide of purpureocobaltia, is thus produced, which unites with acids, and forms a peculiar class of salts: this alkaline solution emits no smell of ammonia.

Fremy, in an elaborate series of researches on the ammoniacal compounds of cobalt, has shown (*Ann. de Chimie*, III. xxxv. 257) that, independently of the ammoniacal compounds obtained with the ordinary salts of the metal, and of the above compounds described by Claudet, three other sets of salts may be procured, which he regards as compounds of different oxides of cobalt with various proportions of ammonia: the first of these bases he names *oxycobaltia*. Its salts crystallize readily; they have for the most part an olive colour, and may be dissolved in a solution of ammonia without change, but when placed in cold water they are decomposed with evolution of oxygen and deposition of a green subsalt: the salts of this base appear to contain a binoxide of cobalt, which, however, cannot be isolated. The second base, from the yellow colour of its salts, he terms *luteocobaltia;* this base has been isolated; it has a strongly alkaline reaction, and its salts crystallize easily. The third base is termed *fuscobaltia;* it forms brown uncrystallizable salts. The base of Claudet's salts, which Fremy termed, from the red colour of its compounds, *roseocobaltia*, is, according to Gibbs and Genth, a mixture of two isomeric bases, one of which, roseocobaltia, neutralizes 3 atoms of a monobasic acid; the other, purpureocobaltia, neutralizes only 2 atoms of acid. Further details regarding the preparation of these different compounds are also contained in a paper by Gibbs and Genth (*Chem. Gaz.*, 1857, p. 181), who have described an additional series, to which they give the name of salts of *xanthocobalt*, from the brilliant yellow colour of these compounds. The chloride of xanthocobaltia ($CoOCl_2$, $5\ H_3N$, $NO_2 + HO$), may be obtained in crystals by decomposing the sulphate of this base with a solution of chloride of barium; and the sulphate (Co_2O_3, $5\ H_3N$, NO_2, $2\ SO_3 + HO$) is easily procured by transmitting a rapid current of nitrous acid through an ammoniacal solution of sulphate of cobalt, taking care to preserve the alkalinity of the liquid by the occasional addition of ammonia. The solution gradually assumes a dark yellowish-brown colour, and if left to evaporate spontaneously deposits the sulphate of the new base in the form of thin plates derived from the right rhombic prism.

All the compounds of each of these bases, when boiled with a solution of caustic potash or of soda, are decomposed, and hydrated sesquioxide of cobalt (Co_2O_3, 3 HO) is precipitated, whilst ammonia is expelled.

The following table will afford a general comparative view of these different classes of salts, including the double salts which ammonia forms with the protoxide of the metal; they are probably compounds, of very complex constitution, formed on the ammonium type:—

1. *Double Salts of Ammonia and Protoxide of Cobalt.*

Nitrate .	$CoO, NO_5, 3\ H_3N, 2\ HO$
Chloride .	$CoCl, \quad 3\ H_3N, 3\ HO$

2. *Salts of Oxycobaltia.*

Nitrate . .	$2(CoO_2, NO_5)\ 5\ H_3N, 2\ HO$
Sulphate .	$2(CoO_2, SO_3)\ 5\ H_3N, 3\ HO$

3. *Salts of Luteocobaltia.*

Nitrate . .	$Co_2O_3, 3\ NO_5, 6\ H_3N$
Chloride .	$Co_2Cl_3, \quad 6\ H_3N$

4. *Salts of Fuscobaltia.*

Nitrate . .	$Co_2O_3, 2\ NO_5, 4\ H_3N, 3\ HO$
Chloride .	$Co_2Cl_2O, \quad 4\ H_3N, 3\ HO$

5. *Salts of Xanthocobaltia.*

Nitrate . .	$Co_2O_3, 2\ NO_5, 5\ H_3N, NO_2 + HO$
Chloride .	$Co_2OCl_2, \quad 5\ H_3N, NO_2 + HO$

6. *Salts of Roseocobaltia (Gibbs and Genth).*

Nitrate . .	$Co_2O_3, 3\ NO_5, 5\ H_3N, 2\ HO$
Chloride .	$Co_2Cl_3, \quad 5\ H_3N, 2\ HO$

7. *Salts of Purpureocobaltia.*

Bisulphate .	$Co_2O_3, 4\ SO_3, 5\ H_3N + 5\ HO$
Chloride .	$Co_2Cl_3, \quad 5\ H_3N.$

(606) Sulphides of Cobalt.—Three sulphides of this metal may be obtained,—a protosulphide, CoS, a sesquisulphide, Co_2S_3, and a bisulphide, CoS_2. The latter may be obtained by heating carbonate of cobalt with sulphur, not allowing the temperature to rise too high. The most important of these is the *protosulphide*, which may be procured in a hydrated condition by precipitating a solution of acetate of cobalt by sulphuretted hydrogen, or by

mixing any neutral solution of a salt of cobalt with hydrosulphate of ammonia. In this form it speedily absorbs oxygen from the air, and becomes converted into sulphate of cobalt. If a mixture of oxide of cobalt with persulphide of potassium (the liver of sulphur) be fused in a covered crucible, a fused sulphide of cobalt is obtained at the bottom of the crucible. The *sesquisulphide,* which is occasionally met with in octohedra of a grey colour, may be obtained by heating sesquioxide of cobalt to about 500° in a current of sulphuretted hydrogen.

(607) CHLORIDE OF COBALT ($CoCl=65$; *Sp. Gr.* 2·937) is obtained as a lilac-coloured anhydrous mass, by passing chlorine over metallic cobalt; it is volatile at a high temperature. By dissolving the oxide or the carbonate of cobalt in hydrochloric acid, the hydrated chloride may be obtained in ruby-red octohedral crystals, which are readily soluble in water and in alcohol; its aqueous solution when concentrated, or when mixed with an excess of strong hydrochloric acid, is of a deep blue colour, but on dilution it becomes pink. This dilute solution may be used as a sympathetic ink; characters traced with it on paper, though invisible when cold, become blue by heat, and again fade as the hygroscopic moisture of the paper is restored from the air: the colours of this ink may be varied at pleasure; the addition of a small proportion of a salt of peroxide of iron renders it green; zinc produces a red, and copper a yellow tint. Anhydrous chloride of cobalt absorbs 2 atoms of ammonia, and if its solution be mixed with an excess of ammonia it deposits crystals, consisting of $CoCl, 3\,H_4NO$.

SULPHATE OF COBALT ($CoO, SO_3+7\,Aq=77{\cdot}5+63$; *Sp. Gr. anhydrous,* 3·531) is isomorphous with sulphate of magnesia.

NITRATE OF COBALT ($CoO, NO_5+6\,Aq=91{\cdot}5+54$) is prepared by dissolving the oxide in nitric acid. It is a deliquescent salt, which is sometimes employed as a reagent for the blowpipe; a fragment of the compound under examination is supported either upon charcoal, or upon a bent platinum wire, and moistened with a minute quantity of a strong solution of the nitrate of cobalt. When treated in this way, many of the compounds of magnesia yield a pale pink-coloured mass after ignition; those of oxide of zinc give a green residue, and those of alumina a blue.

If a concentrated solution of nitrite of potash be gradually added to a solution of nitrate of cobalt acidulated with nitric or with acetic acid, a beautiful orange-yellow compound is precipitated in microscopic four-sided prisms with pyramidal summits: it

is sparingly soluble, and, according to A. Stromeyer, consists of $[Co_2O_3, 2\ NO_3 + 3(KO,NO_3) + 2\ HO]$, and contains 13·6 of metallic cobalt.

A hydrated *arseniate* of cobalt ($3\ CoO, AsO_5 + 8\ Aq$) is found native, in minute crystals, and is known as *cobalt bloom.*

(608) Carbonates of Cobalt.—Cobalt resembles magnesia, zinc, nickel, and copper, in the circumstance that when solutions of its neutral salts are mixed with a solution of carbonate of soda or potash, the precipitate which falls is not a neutral carbonate, but a mixture of neutral carbonate with hydrated oxide of cobalt. If the two solutions be mixed when hot, the red precipitate is said to have the formula ($5\ CoO, 2\ CO_2 + 4\ Aq$). If the salts be mixed at the ordinary temperature, the precipitate is of a brighter red, and has a composition ($4\ CoO, 2\ CO_2 + 7\ Aq$). If either of these precipitates be boiled with an excess of carbonate of soda, it assumes an indigo blue colour, and is converted into the compound $4\ CoO, CO_2 + 4\ Aq$, which absorbs oxygen, and becomes green during washing.

A true neutral carbonate $[3\ (CoO, CO_2) + 2\ Aq]$ is formed by digesting either of the basic carbonates of cobalt with bicarbonate of soda or ammonia.

(609) Characters of the Salts of Cobalt.—The crystallized salts of cobalt are red; when anhydrous they are usually lilac-coloured. Their solutions when in a very concentrated form are blue; at a particular stage of dilution they are red when cold, but become blue on heating them, the red colour returning as the liquid cools: when mixed with a larger proportion of water they exhibit a delicate rose colour, and this tint is perceptible even when the solution is very much diluted. They have an astringent metallic taste.

Before the blowpipe the compounds of cobalt are easily recognised by the intense blue colour which they communicate to a bead of borax in the oxidating flame.

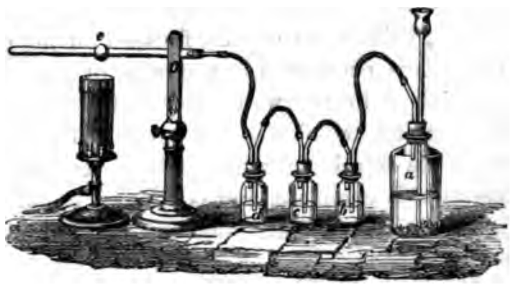
In solution the salts which this metal forms with the mineral acids give no precipitate with *sulphuretted hydrogen*, if the liquid be slightly acidulated with sulphuric or hydrochloric acid; but the cobalt is completely precipitated by it from a dilute neutral solution of the acetate. With *hydrosulphate of ammonia* they yield a black sulphide. *Carbonate of potash* gives a rose-coloured basic carbonate, which is soluble in carbonate of ammonia. *Potash* gives a blue subsalt, which by excess of the alkali becomes rose-coloured.

Ammonia produces a similar effect, but readily dissolves the precipitate, forming a brownish solution which rapidly absorbs oxygen from the air, and becomes red. The soluble *oxalates* give a sparingly soluble pink oxalate of cobalt, which is soluble in nitric acid and in ammonia. *Ferrocyanide of potassium* gives a dirty green, and *ferridcyanide of potassium* a bulky reddish-brown precipitate; the latter reaction occurring even in ammoniacal solutions.

(610) *Estimation of Cobalt.*—Cobalt may be estimated with accuracy in the metallic form. Supposing that no compound of any other metal susceptible of precipitation by sulphuretted hydrogen be present, the solution is to be neutralized by means of carbonate of potash, mixed with a solution of acetate of potash, and the cobalt precipitated as sulphide by a current of sulphuretted hydrogen, the precipitate allowed to settle in a beaker closed by a glass plate, then collected on a filter, and washed. The alkalies are prevented from effecting the complete precipitation of cobalt, as well as of iron, of nickel, of copper, and of many other metals, by the presence of certain kinds of organic matter, such as that derived from the paper of the filter; special precautions are therefore required to avoid this accident. For this purpose the neck of the funnel with the filter and its contents is introduced into a small flask, a hole is made with a glass rod in the bottom of the filter, and the precipitate is washed into the flask; the filter after being moistened with concentrated nitric acid, is again washed; it is then dried, burnt, and the ash added to the contents of the flask, which are now boiled with nitric acid until the sulphide of cobalt is dissolved. The liquid so obtained is diluted and poured off from any particles of undissolved sulphur, and the solution of cobalt may be mixed with sulphuric acid to convert it into sulphate, and evaporated to dryness: 100 parts of sulphate of cobalt indicate 38·06 of the metal. After the sulphide has been brought into solution by the nitric acid, the cobalt may also be precipitated in the form of hydrated oxide by an excess of pure potash; the oxide is then thoroughly washed with boiling water, dried, ignited, and weighed: the black oxide thus procured consists of Co_3O_4, and corresponds to 73·44 of metallic cobalt. Some chemists, however, prefer to reduce this oxide in a current of dry and pure hydrogen in the manner shown in fig. 325. The tube, *e*, is weighed when empty; then a certain proportion of the oxide of cobalt is introduced into the bulb, and the tube is again weighed; hydrogen is generated in the bottle, *a*, and allowed to traverse the vessels, *b*, *c*, and *d*: *b* contains a solution of potash, and *c* one of nitrate of

silver, which are designed to arrest any traces of arseniuretted hydrogen; oil of vitriol is placed in *d* for the purpose of drying the gas: a dull red heat is next applied to the bulb, *e*; under these circumstances the hydrogen enters into combination with the oxygen of the oxide, and the water which is produced passes off as vapour: as soon as water ceases to be formed the reduction is complete: the lamp may then be removed from the bulb, but the current of hydrogen must be maintained till the tube is quite cold. The tube and its contents are finally weighed a third time, and the proportion of metallic cobalt, which a given weight of the oxide under trial contained, is thus ascertained; but the process is not to be recommended, as if the tube be weighed full of hydrogen, the weight is too little, and if the hydrogen be displaced by atmospheric air, the reduced metal is apt to become partially oxidized.

FIG. 325.



(611) *Separation of Cobalt from the Alkalies and Alkaline Earths, and from Alumina.*—This is readily effected by converting the cobalt into acetate, and transmitting sulphuretted hydrogen, as has been already mentioned in the preceding paragraph. Another plan consists in the addition of hydrosulphate of ammonia to the solution previously neutralized by ammonia. If alumina be present, it will accompany the cobalt, but if this precipitate be redissolved in acid, and again thrown down by means of caustic potash in excess, the alumina will be retained; the oxide of cobalt is, however, apt to carry down traces of alumina; these may be removed by treating the precipitated oxide by means of a mixture of ammonia and chloride of ammonium, which dissolves the cobalt, but leaves any traces of alumina which may have accompanied it. The cobalt is again precipitated by hydrosulphate of ammonia.

The separation of Cobalt from Zinc is not easy. One of the best methods consists in precipitating the two metals together in the form of sulphides, dissolving this precipitate in nitric acid, and then adding an excess of carbonate of potash, and evaporating to dryness. After the mixed carbonates of zinc and cobalt have

been well washed, they are heated in a bulb-tube in a current of dried hydrochloric acid: in this process the carbonic acid is expelled, and the metals are converted into chlorides whilst water is formed. The open end of the tube is in this case bent downwards at a right angle, and the aperture is made to dip into a small quantity of water contained in a flask; the chloride of zinc, which is volatile, is carried forward in the current of gas, a portion of it is condensed in the bend of the tube, and the remainder is dissolved in the water placed for its reception. Chloride of cobalt alone remains in the bulb. The portion of the tube in which the chloride of zinc has been condensed is cut off when the operation is complete, and is allowed to fall into the flask. The zinc and the cobalt are then easily determined separately by the usual methods.

§ IV. NICKEL (Ni=29·5); *Sp. Gr.* 8·82.

(612) NICKEL is a metal, the peculiar characters of which were first recognised in 1751 by Cronstedt; it has a remarkable analogy with cobalt, and always occurs associated with it in nature, both as a constituent of meteoric iron, and in its ores, which present a composition similar to those of cobalt. It is most abundant in the form of kupfernickel, which is a diarsenide of nickel, and is extracted either from this ore or from *speiss*, which is an impure arseniosulphide of nickel, formed during the manufacture of smalt (604).

Preparation.—As the metal itself is now extensively used in alloys, of which German silver is one of the most important, great pains have been taken to procure it in a state of comparative purity, and several processes have been proposed.

1.—According to Louyet, the method by which nickel is extracted from speiss at Birmingham on the large scale is as follows:—The speiss is first fused with chalk and fluor-spar, the metalliferous mass so obtained is reduced to powder, and roasted for twelve hours to expel the arsenic; the residue is next dissolved in hydrochloric acid; the solution is diluted, and the iron peroxidized by the cautious addition of bleaching powder. Milk of lime is then carefully added so long as peroxide of iron falls, which carries down with it the last portions of arsenic: this precipitate is well washed, and the liquid, which contains all the cobalt and nickel, is treated with a current of sulphuretted hydrogen; the sulphides of copper, bismuth, and lead, are thus precipitated, and are thoroughly washed. All the nickel and cobalt still remain in the liquid; this liquid is

boiled to expel sulphuretted hydrogen, neutralized with lime, and is again treated with chloride of lime: the whole of the cobalt is thus thrown down as peroxide; after which the whole of the nickel is separated from the solution in the form of hydrated oxide by adding milk of lime so long as any precipitate is produced.

2.—Nickel may be obtained pure upon a small scale, by dissolving the roasted ore in aqua regia, evaporating to expel the excess of acid, redissolving in water, and transmitting a current of sulphuretted hydrogen. The filtered liquid is boiled with nitric acid, to peroxidize the iron; the solution is precipitated by an excess of caustic ammonia, filtered from the oxide of iron, and to the blue liquid caustic potash is added until the blue tint nearly disappears; a pale green precipitate, consisting of hydrated oxide of nickel and potash is thus obtained, which must be well washed with hot water to remove the potash, and then reduced by ignition in a current of hydrogen gas: when obtained in this manner it is generally pyrophoric. If heated for an hour by means of a blacksmith's forge, in a crucible lined with charcoal, a well-fused button of carbide of nickel is produced. A button of the pure metal may however be procured by heating the oxalate of nickel intensely in a crucible with a luted cover, without any other reducing agent than the carbonic oxide furnished by its own decomposition.

3.—It may also be obtained in laminæ by the electrolysis of a solution of the double sulphate of nickel and ammonia.

Properties.—Pure nickel is a brilliant, silver-white, hard, but ductile metal, little more fusible than iron, which, according to Deville, it even surpasses in tenacity. At ordinary temperatures it is susceptible of magnetism, but it loses this property almost entirely if heated to a point exceeding 630°, though it recovers its magnetic power on cooling. Nickel becomes oxidized by exposure to a current of air at a high temperature. The metal is easily attacked at ordinary temperatures by chlorine or bromine if suspended in water. It is also readily dissolved by nitric acid and by aqua regia, and is dissolved slowly with evolution of hydrogen by diluted sulphuric or by hydrochloric acid. Owing to the remarkable whitening power which nickel exerts on brass, it is now much used in the manufacture of *packfong*, or German silver, a compound of zinc, nickel, and copper, in which the proportions of the metals may vary considerably. A good alloy consists of 5 equivalents of copper, 3 of zinc, and 2 of nickel, or, in 100 parts, of 51 of copper, 30·6 of zinc, and 18·4 of nickel. Packfong is of a yellowish-white colour, and when freshly polished closely resembles silver in appearance. *Tutenag* is the name given by the Chinese

to a similar alloy, consisting of 8 parts of copper, 6¼ of zinc, and 3 of nickel.

The native arsenides of nickel are important, as they form the principal ores of the metal. *Kupfernickel* (Ni_2As) is a diarsenide of nickel; it contains 44 parts of nickel to 56 of arsenic; part of the arsenic in this ore is sometimes displaced by an equivalent amount of antimony. It has a reddish colour, and a metallic lustre. It is not attacked by hydrochloric acid, but is soluble in nitric acid, and is decomposed when heated in air or in a current of chlorine. *Arsenical nickel* is a combination of an atom of each metal (NiAs): by ignition in closed vessels it loses half its arsenic, and becomes converted into kupfernickel. A compound of nickel with arsenic and sulphur, corresponding to mispickel, and known as *nickel glance* (NiS_2,NiAs), is also found native.

(613) Oxides of Nickel.—Nickel forms two oxides; a protoxide, NiO, and a sesquioxide, Ni_2O_3.

The Protoxide (NiO=37·5; *Sp. Gr.* 5·74) may be obtained in the anhydrous form by igniting the nitrate or the carbonate of the metal in a covered crucible, when it is left of an olive-green colour. It may be precipitated from its salts by potash, as a bulky light-green hydrate (NiO,HO), and may be obtained crystallized by decomposing the solution of carbonate of nickel in ammonia by ebullition. Oxide of nickel is readily soluble in acids, forming salts which have a pale green colour. It forms insoluble compounds with potash and with soda, which, however, may be decomposed by frequent washings with boiling water. Baryta, strontia, and several other bases, also form with it insoluble compounds; ammonia dissolves it, forming a deep blue solution. A solution of hydrochlorate of ammonia also dissolves it slowly.

The Sesquioxide (Ni_2O_3=83) is a black powder which may be procured as a hydrate with 5 Aq, by treating the hydrated protoxide with a solution of chloride of soda. It does not combine with acids, and gives off a portion of its oxygen by ignition, or by heating it with nitric or sulphuric acids, which form with it salts of the protoxide.

(614) Sulphides of Nickel.—Three of these compounds are known; a disulphide, a protosulphide, and a bisulphide. The *protosulphide* (NiS=45·5) occurs native in greyish or yellowish capillary crystals, which are insoluble in hydrochloric, but soluble in nitric acid: it may be formed artificially by fusion of sulphur with nickel. It may also be procured by fusing a persulphide of one of the alkaline metals with arsenide of nickel, and is left in yellow crystalline scales. A black

hydrate of this sulphide is produced when a salt of nickel is precipitated by sulphide of ammonium; in this form it absorbs oxygen from the air, and is gradually converted into sulphate of nickel. The *disulphide* (Ni_2S) may be formed by reduction of the sulphate of nickel by means either of charcoal or of hydrogen gas. The *bisulphide* (NiS_2) is left as a steel-grey powder on treating with water the mass obtained by heating to redness an intimate mixture of carbonate of nickel, carbonate of potash, and sulphur.

Chloride of Nickel ($NiCl=65$) is formed by dissolving the oxide in hydrochloric acid. Its solution, on evaporation, yields green hydrated crystals with 9 Aq; by heat it may be obtained as a yellowish-brown anhydrous mass, which at a high temperature is volatile, and condenses in yellow crystalline scales, which are dissolved slowly by boiling water. If heated in a current of air, a portion of the chlorine is expelled, and a corresponding quantity of oxide of nickel is formed.

Sulphate of Nickel ($NiO,SO_3+7Aq=77{\cdot}5+63$); *Sp. Gr. cryst.* 2·037.—This salt may be obtained by dissolving metallic nickel, or its oxide or carbonate, in sulphuric acid. It crystallizes in green rhombic prisms, which require 3 parts of cold water for solution: the prismatic crystals, when exposed to light, are converted into small regular octohedra, aggregated together in the form of the original crystal, which becomes opaque. It may be obtained in octohedra at once with 6 Aq (Pierre), by crystallizing at a temperature between 60° and 80°. *A double sulphate of potash and nickel* (NiO,SO_3+KO,SO_3+6Aq; *Sp. Gr. anhydrous* 2·897, *cryst.* 2·190) may be formed by adding potash to the impure solution of speiss, and by repeated crystallizations may be freed from all impurities except traces of iron and cobalt: it was at one time used as a means of purifying nickel for commercial purposes. Other double sulphates of nickel may be formed. Sulphate of nickel in the solid form absorbs 3 atoms of ammoniacal gas. An insoluble *basic sulphate* is obtained by adding to a solution of the neutral sulphate a quantity of potash insufficient for its complete decomposition.

Carbonates of Nickel.—There are several basic carbonates of nickel, of a green colour. The neutral carbonate is precipitated as a crystalline powder, when a solution of nitrate of nickel is poured into a large excess of bicarbonate of soda.

(615) Characters of the Salts of Nickel.—The salts of this metal are of a delicate green colour, both when in the solid

state and when in solution; they redden blue litmus feebly. They have a sweetish astringent metallic taste, and when taken internally excite vomiting.

Before the blowpipe, salts of nickel give in the oxidating flame with borax a reddish-yellow glass, which becomes much paler as it cools. The addition of a salt of potash colours the bead blue. In the reducing flame, greyish particles of reduced nickel are disseminated through the bead.

In solution, *sulphuretted hydrogen* gives no precipitate if the liquid be acidulated with sulphuric acid; but it precipitates a diluted solution of acetate of nickel, if nearly neutral, very perfectly when aided by a gentle heat. *Hydrosulphate of Ammonia* gives a black sulphide slightly soluble in excess of the precipitant, forming a dark-brown solution. *Ammonia* gives a pale green precipitate, soluble in excess of ammonia, forming a bright blue solution, from which an excess of potash precipitates a green compound of oxide of nickel and potash. *Potash* and *Soda* throw down a pale-green bulky hydrated oxide of nickel, insoluble in excess of the alkali. The *carbonates of the alkalies* give a pale apple-green precipitate of basic carbonate of nickel, which is readily soluble in carbonate of ammonia. *Ferrocyanide of potassium* gives a greenish-white, and *ferridcyanide of potassium* a yellowish-green precipitate, both of which are soluble in hydrochloric acid.

Binoxalate of Potash in a neutral solution, if not too dilute, causes the deposition of a greenish-white sparingly soluble double oxalate of nickel and potash, soluble in excess of ammonia.

(616) *Estimation of Nickel.*—Nickel is best estimated in the form of protoxide which, when precipitated by means of potash, requires patient washing with hot water to remove the adhering alkali: 100 parts of protoxide of nickel contain 78·69 of the metal.

Separation of Nickel from the Alkalies and Earths, and from Zinc.—For this purpose the same processes as those adopted for the separation of cobalt (611) may be employed.

(617) *Separation from Cobalt.*—The following method advised by Liebig, and slightly modified by Hadow, is the best for this purpose. The nitric solution of the cobalt and nickel having been freed from all other metals except potassium or sodium, after being nearly neutralized, is mixed with an excess of hydrocyanic acid, and then with pure caustic potash, or carbonate of potash, after which the mixture is boiled for ten minutes. During this time oxygen is absorbed, and the liquid acquires a pale yellow colour. A cobalticyanide of potassium ($K_3Co_2Cy_6$) is formed, and a double

cyanide of nickel and potassium (KCy + NiCy) is produced at the same time. The formation of the cobalticyanide may be traced as follows: cyanide of cobalt is first formed (HCy + CoO = CoCy + HO), and this cyanide of cobalt, by boiling with an excess of cyanide of potassium and hydrocyanic acid, yields cobalticyanide of potassium, whilst oxygen is absorbed and water is separated; $2\,CoCy + 3\,KCy + HCy + O = (K_3Co_2Cy_6) + HO$. The double cyanide of nickel and potassium is very simply formed; for with nickel no compound corresponding to the cobalticyanide is obtained; $2\,KCy + NiO = (KCy,NiCy) + KO$. If the strongly alkaline solution be now boiled with a solution of pernitrate of mercury added in slight excess, so as to produce a precipitate, which from its yellowish colour shows that the oxide of mercury is in excess, the nickel salt is decomposed, hydrated oxide of nickel is precipitated, and cyanide of mercury is produced:—$(KCy,NiCy) + HgO = (KCy,HgCy) + NiO$.

The cobalticyanide of potassium is not decomposed by the oxide of mercury, but remains in solution, and may be filtered from the oxide of nickel, which requires to be carefully ignited in a platinum crucible till it ceases to lose weight. After carefully neutralizing the filtrate with nitric acid, the cobalt may then, by the addition of a solution of subnitrate of mercury, be precipitated as a white subcobalticyanide of mercury: the precipitate is collected, dried, and ignited, when pure oxide of cobalt is left.

If, instead of precipitating the mixed cyanides by means of mercury, a solution of chloride of soda be added in excess to the boiling alkaline liquid, in quantity sufficient to destroy the free cyanide of potassium, the nickel is precipitated of an intense black as sesquioxide, in which form it may be readily washed, and by ignition it may be converted into the protoxide, in which state it may be weighed. Traces of nickel which escape discovery by other methods may thus often be detected in cobalt. Care must be taken to ascertain the absence of manganese, as it would go down with the nickel, accompanied by traces of iron, if the latter metal were present.

§ V. URANIUM (U=60). *Sp. Gr.* 18·4.

(618) URANIUM is a metal the compounds of which are but sparingly distributed over the surface of the earth. It was originally discovered by Klaproth, in *pitchblende*, which contains nearly 80 per cent. of the black oxide of uranium ($2\,UO,U_2O_3$); the remainder of the mass consists of variable quantities of copper, lead, iron, arsenic, and frequently of cobalt and nickel. *Uranite*, which is a mineral of micaceous structure, of rarer occurrence, consists of

a hydrated double phosphate of lime and uranium ($CaO, 2\ U_2O_3, PO_5 + 8\ Aq.$) *Chalcolite* ($CuO, 2\ U_2O_3, PO_5 + 8\ Aq$) is a similar mineral, in which oxide of copper takes the place of lime.

In order to extract uranium from pitchblende, the mineral is heated to redness, and thrown whilst red-hot into water, after which it admits of being readily pulverized: Ebelmen then treats the ore in the following manner :—The fine powder is washed with diluted hydrochloric acid, heated with charcoal, and digested in strong hydrochloric acid, by which the earthy matters and most of the iron, arsenic, and sulphur are removed: the washed residue is roasted and then treated with nitric acid; the solution thus obtained is evaporated nearly to dryness, to expel the excess of acid, and is diluted, by which means the arseniate of iron is precipitated. Sulphuretted hydrogen is then transmitted through the filtered solution, and the liquid is filtered from the sulphides of copper, lead, and arsenic thus thrown down; after which it is again evaporated until crystals of pernitrate of uranium begin to be formed. This salt is decomposed by heating it to redness, and the oxide of uranium which is left is mingled with charcoal and heated in a glass tube through which a current of dry chlorine is passing; carbonic acid and carbonic oxide are thus formed, and a volatile green protochloride of uranium sublimes. This chloride, when heated with potassium in a platinum crucible, yields chloride of potassium and metallic uranium: intense heat is evolved during the reaction of the potassium on the chloride of uranium, and the resulting metal is partially fused. The isolation of metallic uranium is due to Péligot (*Ann. de Chimie*, III. v. 5), the substance originally supposed to be the metal having been proved by him to be its protoxide.

Uranium as thus obtained is of a steel-white colour: it appears to be slightly malleable; it is not oxidized by exposure to air or to water at ordinary temperatures; but if heated in the air it burns brilliantly: sulphuric and hydrochloric acids dissolve it with extrication of hydrogen gas. In its chemical relations it is somewhat analogous to iron and manganese.

(619) OXIDES OF URANIUM.—Uranium forms two principal oxides, a *protoxide*, UO, and a *sesquioxide*, U_2O_3: two intermediate oxides may also be obtained, the *black oxide*, $2\ UO, U_2O_3$, and the *green oxide*, UO, U_2O_3.

The *Protoxide* ($UO = 68$) may be obtained in several ways; one of the easiest consists in igniting the peroxalate in closed vessels, or in a current of hydrogen. In its anhydrous state the dilute acids are without action upon it, but its hydrate, which may be

obtained in reddish-brown flocculi, by adding ammonia to a solution of the protochloride, is readily soluble in the acids; it forms green crystallizable salts, which have a strong tendency to absorb oxygen.

The *Black Oxide* ($2\,UO,U_2O_3$) may be procured by heating the protoxide to bright redness, and suddenly cooling it, or by igniting the pernitrate of uranium. It furnishes a pure and intense black, highly prized for colouring porcelain.

The *Green Oxide* (UO,U_2O_3), which corresponds in composition to the magnetic oxide of iron, is procured by heating the black oxide moderately in a current of oxygen or in the open air; by more intense ignition it becomes re-converted into the black oxide, and is again partially re-oxidized as it cools. It is soluble in hot concentrated sulphuric acid, but does not form distinct salts.

The *Sesquioxide* or *Peroxide* (U_2O_3) performs the part both of an acid and of a base. It is with difficulty obtained in a pure state. By exposing the peroxalate of uranium to the sun's rays, a brownish-violet powder, which is a hydrate of the green oxide, is deposited, while carbonic acid makes its escape; this precipitate absorbs oxygen on exposure to the air, and becomes converted into a greenish-yellow mass, which, according to Ebelmen, is a hydrate of the sesquioxide (U_2O_3, $2\,HO$). The sesquioxide may be obtained in the anhydrous state as a brick-red powder, by heating this hydrate to a temperature not exceeding 572°. Peroxide of uranium combines readily with acids, and forms salts of a bright yellow colour. If an attempt be made to procure the peroxide by decomposing the solutions of these salts by the addition of an alkali, an insoluble yellow precipitate, consisting of a compound of the sesquioxide of uranium with the alkali, frequently called a *uranate* of the base, falls; uranate of potash has the formula KO, $2\,U_2O_3$, and the other similar compounds have a corresponding composition; this compound cannot be decomposed even by boiling water: the commercial yellow oxide is a hydrated uranate of ammonia, from which heat expels the water and ammonia, and also converts the peroxide into the black or the green oxide. The compounds of the peroxide of uranium with the earths, however, stand a strong heat without decomposition, and are employed to communicate a beautiful and peculiar yellow to glass.

(620) Chlorides of Uranium.—The *Protochloride* (UCl) is a green, volatile, deliquescent compound, which is decomposed by water; the method of preparing it has already been described (618). If dry hydrogen gas be transmitted over the protochloride of uranium while it is being heated to redness in a glass tube, a

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subchloride (U_4Cl_3) is produced, which crystallizes in slender dark-brown needles, which are but slightly volatile; they are very soluble in water, and form a deep purple solution, from which ammonia throws down a brown suboxide; this oxide absorbs oxygen from the air rapidly. An *oxychloride* (U_2ClO_2), or ($2\ U_2O_3$, U_2Cl_3), somewhat analogous to chlorochromic acid (657), is formed by passing chlorine over the protoxide of the metal; it is deliquescent, and forms a yellow solution with water; with the chlorides of the alkaline metals it forms remarkable double salts; the double salt with chloride of potassium consists of ($KCl,U_2ClO_2 + 2\ Aq$), and crystallizes in rhombic tables of a greenish-yellow colour.

(621) CHARACTERS OF THE COMPOUNDS OF URANIUM.—1. The *salts of the protoxide* of uranium have a green colour, and have a strong tendency to form double salts with salts of the alkaline metals which contain the same acid as themselves. In solutions of the protosalts of uranium *ammonia* and the *alkalies* give a gelatinous, blackish-brown precipitate of hydrated oxide; this precipitate absorbs oxygen and becomes yellow from the formation of sesquioxide of uranium, which unites with the excess of alkali. *Sulphuretted hydrogen* produces no precipitate; but *hydrosulphate of ammonia* occasions a black deposit of sulphide of uranium. *Oxalate of ammonia* gives a greenish-white precipitate of oxalate of uranium. Solutions of the green salts of uranium absorb oxygen rapidly, and are converted by nitric acid into persalts, even without the aid of heat.

2.—*The salts of the peroxide* are yellow, and all of them contain, even when crystallized from strongly acid solutions, 1 atom of sesquioxide to 1 atom only of the acid. The pernitrate, for instance, which crystallizes in long striated prisms, consists of ($U_2O_3,NO_5 + 6\ Aq$). Numerous double salts of this oxide have also been formed: the persulphate of uranium and potash consists of ($KO,SO_3 + U_2O_3,SO_3 + 2\ Aq$). Solutions of the persalts of uranium give with *ammonia* a yellow precipitate, consisting of uranate of ammonia; with *ferrocyanide of potassium* they yield a hair-brown precipitate. By the action of ammonia they are distinguished at once from the compounds of copper, which give a blue solution on the addition of an excess of ammonia, though they yield a precipitate with the ferrocyanide similar in colour to that furnished by the salts of uranium. *Sulphuretted hydrogen* produces no precipitate, but *hydrosulphate of ammonia* gives a yellowish brown sulphide. *Carbonates of the alkalies* give a yellow, granular preci-

pitate, soluble in excess of the precipitant; these precipitates are double carbonates of uranium and of the alkali employed. With *infusion of nut galls* a dark-brown precipitate is produced.

(622) *Estimation of Uranium.*—Uranium is usually estimated in the form of protoxide, to which it is reduced by heating the sesquioxide to redness in a glass tube in a current of hydrogen; the tube must be sealed up whilst full of hydrogen, and weighed in this condition, to prevent the oxide from reabsorbing oxygen from the air.

Uranium is separated from the alkalies by converting it into a persalt by nitric acid, if not already in that condition, and then precipitating it in the form of yellow uranate of ammonia. If baryta, strontia, lime, or magnesia be present, the addition of sulphuric acid separates the first two bases in the form of sulphates; if lime or magnesia be present, the solution is filtered from the precipitate, the filtrate evaporated to dryness, and then heated with alcohol of specific gravity 0·900; the sulphates of lime and magnesia remain unacted upon, whilst the persulphate of uranium is dissolved.

Alumina, glucina, zinc, cobalt, and nickel, may be separated from uranium by adding bicarbonate of potash to the acidulated solution: a double carbonate of potash and uranium remains in the liquid, whilst the earths, and other metallic oxides, are precipitated. For the success of this experiment it is necessary, if the salts of ammonia be present, that they should be expelled, by evaporating the solution to dryness and igniting the residue, before effecting the precipitation of the various bases with bicarbonate of potash.

§ VI. Iron (Fe=28). *Sp. Gr.* 7·844.

(623) *Condition of Iron in Nature.*—Iron is more extensively diffused than any other metal: not only is it abundant in the inorganic creation, but it is an essential constituent in the blood of the vertebrate animals.

Iron has been occasionally found in the native form accompanying the ores of platinum; but when it occurs in the metallic state it is generally met with in meteoric masses associated with nickel, cobalt, and small quantities of other metals, among which are copper, manganese, and chromium. Some of these masses which have fallen in an ignited state from the atmosphere are of very considerable size. One discovered in Siberia, by Pallas, weighed 1600 lb., and a block found in the district of Chaco-Gualamba, in South America, is estimated at between 13 and 14 tons weight. These extraordinary bodies are unimportant as sources of iron.

The ores of iron are numerous. The most valuble are the following:—

1.—*Magnetic Iron Ore,* or *Loadstone* (FeO,Fe_2O_3; *Sp. Gr.* 5·09). This is found in enormous masses, or even mountains, amongst the primary formations. Much of the best Swedish iron is obtained from this material, which is also abundant in North America. Occasionally it is found in detached octohedral crystals. Coal is absent in those formations in which this mineral is found; hence charcoal is the fuel ordinarily employed in smelting it. This fuel contains a smaller amount of ash than coal; fewer impurities are therefore introduced by it during the smelting than when coal is used; and as the ore itself is generally very pure, the metal which it furnishes is of excellent quality. The *iron sand,* found in India, and employed in the manufacture of wootz, consists chiefly of magnetic oxide of iron.

2.—*Specular Iron Ore,* or *Fer Oligiste; Sp. Gr.* 5·2.—This is an anhydrous sesquioxide of iron (Fe_2O_3): it occurs in the primary rocks. The principal part of the celebrated Elba iron, and also a large quantity of Russian and of Swedish iron, are obtained from this source. Charcoal is in this case also the fuel employed.

3.—*Red Hæmatite* (Fe_2O_3, *Sp. Gr.* about 5·0) is another form of the anhydrous peroxide: it is sometimes found massive, but more generally in fibrous crystalline nodules. This ore is largely raised in Lancashire and in some parts of Cornwall. It is seldom smelted alone; but it forms a valuable addition to the clay ironstone of the coal measures.

4.—*Brown Hæmatite* ($2\ Fe_2O_3, 3\ HO$); *Sp. Gr.* about 3·9.—This is a hydrated peroxide of iron, which generally occurs massive. It is, however, also met with in the oolitic strata, in some parts of France, in the form of rounded masses termed *pea iron ore,* mixed with a small proportion of clay. Much of the French iron is obtained from this source. Brown hæmatite is readily soluble in hydrochloric acid; it is less refractory in the furnace than the preceding variety. The brown hæmatite, when roasted, becomes porous from the loss of its water, and is thus rendered more manageable. Mixed with variable proportions of earth or clay, and sometimes with oxide of manganese, this oxide of iron forms the varieties of umber and ochres. It occurs principally in the secondary and tertiary deposits.

5.—*Spathic Iron,* or *Carbonate of Iron* (FeO,CO_2); *Sp. Gr.* 3·8. —This is found in crystalline masses often combined with carbonate of magnesia and with a considerable proportion of manganese,

as in the Saxony ores. Much of the so-called *natural steel* is made from this ore.

6.—*Clay Ironstone* is the chief source of the enormous quantity of iron manufactured in Great Britain. It is an impure carbonate of iron, containing generally from 30 to 33 per cent. of metallic iron, mingled with varying proportions of clay, oxide of manganese, lime, and magnesia. This argillaceous ironstone occurs in bands broken up into nodules, or in continuous seams, from two to fourteen inches thick, alternating with beds of coal, clay, shale, or limestone, in the coal measures, diffused over large areas in South Staffordshire, South Wales, and some other parts of Great Britain. It is also found in the United States, and in Bohemia and other countries of central Europe. It has a specific gravity ranging between 2·7 and 3·47.

7.—*The Black Band* of the Scotch coal fields is also a carbonate of iron, but the principal foreign matter in this mineral, which often amounts to 25 or 30 per cent., is of a bituminous or combustible nature.

8.—A siliceous ironstone has been found abundantly in the oolite in the neighbourhood of Northampton. It yields an inferior iron, owing to the presence of a large quantity of phosphates in the ore.

9.—Another, but comparatively an unimportant ore, of a brown colour, known as *bog-iron ore*, is a mixture of hydrated peroxide and phosphate of iron in variable proportions. It occurs in marshy, alluvial districts, near the surface.

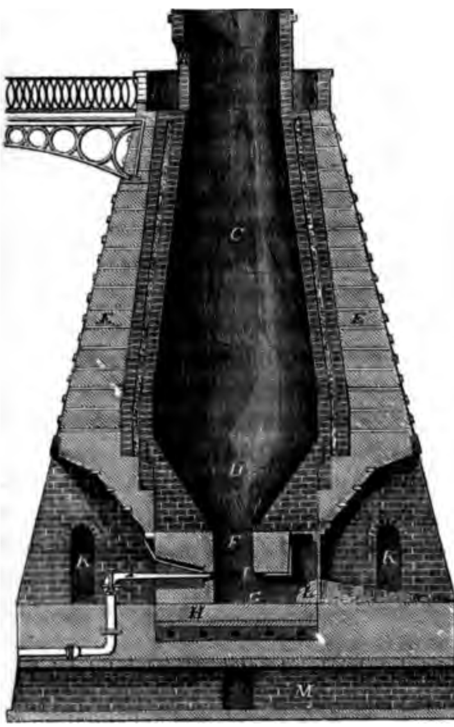
Iron pyrites (FeS_2), though a very abundant mineral, is wrought only for the sake of its sulphur, because the iron which it furnishes is not pure enough for use.

(624) Smelting of Clay Ironstone.—After the ore has been broken up into masses about the size of two fists, it is roasted, in order to expel water and carbonic acid; the mass is thus left in a porous state, highly favourable to its subsequent reduction in the furnace. The roasting is sometimes performed in kilns, but usually in heaps in the open air. If this operation is to be effected in the open heap, a plat of ground is levelled and covered with a layer of coal in lumps to the depth of 10 or 12 inches; this is succeeded by alternate layers of the mineral and of small coal. The quantity of coal required in the case of the black band is often very small, as the ore itself frequently contains sufficient inflammable matter to continue burning when once well lighted. The heap, when finished, is 14 or 15 feet wide, 8 or 10 high, and

of great length. The fire is kindled at the windward extremity, and allowed to spread gradually through the mass. This preliminary operation occupies some months for its completion. The roasted ore is then ready for the smelting.

The *blast furnace* employed for this purpose is represented in section in fig. 326. The internal cavity in shape resembles a long narrow funnel inverted upon the mouth of another shorter funnel. These furnaces are usually about 50 feet high, and from 14 to 17 feet in diameter in the widest part of the cavity. The lowest portion, F, or neck of the funnel, is termed the *crucible,* and is made of very refractory gritstone. In the front, 8 or 10 inches from the floor or *hearth,* H, is a longitudinal aperture above the *tymp-stone,* L, for the overflow of the slag, and on the sides are the openings for the *tuyères,* I I, or blast-pipes, which are connected with powerful blowing machines for supplying air under a pressure of from 2 lb. to 3 lb. upon the inch. A steady and most intense heat in thus uniformly maintained. At the lowest point of the furnace is the *tap-hole,* for drawing off the melted metal at suitable intervals, and which, except at such times, is closed with sand and clay: K K, are galleries, which allow the workmen free access to the tuyères and lower portion of the furnace, the base of which is kept dry and well drained by the arched channels, M. Above the crucible the furnace suddenly widens, forming the *boshes,* D; the lining, C, is formed of fire-bricks, which are continued up to the throat, A, of the furnace: the whole is cased in solid masonry, E E, and supported by iron bands. When working regularly, such a furnace is charged through the opening, B,

FIG. 326.



near the top, at intervals, first with coal, and then with a suitable mixture of roasted ore and of a limestone flux broken into small fragments. As the fuel burns away, and the materials sink down gradually, fresh layers of fuel, and of ore, are added; so that the furnace becomes filled with alternate layers of fuel and of ore.

The principal substances which are acted upon in such a furnace are the following:—

1st, The oxygen contained in the air of the blast; 2nd, the roasted ore,—consisting of oxide of iron, silica in the shape of sand or quartz, clay or silicate of alumina, and a little magnesia and oxide of manganese; 3rd, coal or coke,—composed chiefly of carbon, with a small proportion of hydrogen; and 4th, carbonate of lime, which in the heat of the furnace soon becomes quicklime.

(625) *Theory of the Blast Furnace.*—The chemical changes may be traced as follows, beginning at the bottom of the furnace:— The oxygen contained in the air of the blast, as soon as it comes into contact with the fuel in the crucible, combines with the carbon and forms carbonic acid, attended with a combustion of intense activity. The blast is thus soon deprived of all its free oxygen; nearly the whole of the nitrogen escapes unchanged, but the carbonic acid, in its passage over the ignited fuel, is decomposed; it combines with an additional equivalent of carbon, and becomes converted into carbonic oxide; for each volume of carbonic acid 2 volumes of carbonic oxide are produced. This formation of carbonic oxide is attended with a large absorption of heat, so that the temperature of the furnace, above the crucible, becomes rapidly reduced, and a quantity of highly combustible gas is thus formed.* This carbonic oxide becomes mingled with carburetted hydrogen and free hydrogen, which are derived from the fuel contained in the upper part of the charge, as it gradually descends towards the focus of intense heat below. A proportion of the gases which escape from the opening at the top of the

* Bunsen and Playfair, in their examination of the gases produced in a hot-blast furnace at Alfreton, found that a considerable amount of cyanide of potassium was formed in the hotter portions of the furnace (*British Association Reports*, 1845, p. 182): part of the nitrogen, derived probably both from the blast and from the coal, had therefore entered into combination with carbon, and had united with the potassium contained in small quantities in the ore and in the ashes of the coal.

The furnace in which these experiments were made was 40 feet deep from the top of the charge to the hearthstone, and was charged every twenty minutes with 420 lb. of ironstone, 390 lb. of coal, and 170 lb. of limestone: each charge yielded 140 lb. of pig iron. The blast was under a pressure of 6·75 inches of mercury.

These chemists state that at a depth of 2¾ feet from the tuyère, or 34 feet from the top of the furnace, the gases which they collected contained 1·34 per

furnace, varying from 35 to 40 per cent., is combustible; the remainder consists principally of nitrogen, with a small amount of carbonic acid. The ore having been rendered porous by the previous roasting, is easily penetrated by these ascending gases, by contact with which the iron becomes reduced in the upper part of the boshes, where the heat is comparatively moderate. By degrees the reduced metal, mixed with the earthy matter of the ore, sinks down to the hotter region. Here the earthy matters melt and become vitrified; whilst the iron, in a minutely divided state, being brought into contact with the carbon of the fuel, combines with it and forms the fusible compound well known as cast iron. This carbide of iron melts, sinks down below the tuyères through the lighter vitrified slags, and is protected by them from the further action of oxygen. The bulk of the slag is 5 or 6 times as great as that of the iron produced: it floats above the melted metal, and is allowed to flow over continually at the opening left for the purpose; whilst the iron is run off at intervals of 12 or 24 hours, by withdrawing the stopping of clay or sand from the tap-hole at the bottom.

The furnace slags constitute an imperfect species of glass, consisting principally of silicates of lime, magnesia, and alumina, with generally a small proportion of silicate of manganese. In the formation of these slags the siliceous matters of the ore act like a true

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cent. of cyanogen. The following table furnishes a summary of the results which they obtained:—

Analysis of Gases from a Hot-blast Furnace.

Depth from the top Height from tuyère .	5 feet. 32	8 29	14 23	17 20	20 17	24 13	34 2¾
Nitrogen	55·35	54·77	50·95	55·49	60·46	56·75	58·05
Carbonic acid . . .	7·77	9·42	9·10	12·43	10·83	10·08	0·00
Carbonic oxide . .	25·97	20·24	19·32	18·77	19·48	25·19	37·43
Light Carb. Hydn. .	3·75	8·23	6·64	4·31	4·40	2·33	0·00
Hydrogen	6·73	6·49	12·42	7·62	4·83	5·65	3·18
Olefiant gas . . .	0·43	0·85	1·57	1·38	0·00	0·00	0·00
Cyanogen	0·00	0·00	0·00	0·00	0·00	trace	1·34
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

The process of coking, which is effected in the upper part of the furnace, did not appear to be complete until the charge had reached a depth of 24 feet, but was most active at a depth of 14 feet; the principal reduction of the ore seemed to take place just below the point at which the coking was completed; the maximum heat of this furnace occurring between about 3 and 4 feet above the tuyère, or 33 feet from the top.

In a furnace fed with charcoal, Bunsen found the reduction of the ore to commence nearer the throat of the furnace, for in this case no absorption of heat occurred similar to that occasioned by the process of coking the coal, which takes place in the upper part of the hot-blast furnace. The body of a charcoal furnace consequently does not require to be so high as that of a furnace in which coal is used. Similar experiments by Ebelmen lead to conclusions substantially the same.

acid, as they combine with the earthy bases, lime, magnesia, and alumina, and really neutralize them.

The general composition of these slags may be seen from the subjoined analysis, by Berthier, of a slag from Merthyr Tydvil:—

		Oxygen.
Silica	40·4	=21·5
Lime	38·5	
Magnesia	5·2	=13·9
Oxide of Iron	3·8	
Alumina	11·2	=5·22
Sulphur	traces	
	99·0	

The composition of this slag may therefore be represented by the formula, $5\ [3\ (CaMgFe)O,\ 2\ SiO_2] + 2\ (Al_2O_3,\ SiO_2)$; the oxygen in the bases being nearly equal in amount to that contained in the silica.

The iron as it runs from the furnace, however, is not a pure carbide or carburet, for in the intense heat, not only is the iron reduced, but portions also of silicon, aluminum, and calcium, and occasionally other bodies derived from the flux and from the fuel. These bodies enter in minute quantity into combination with the iron, the properties of which they materially modify. Manganese generally accompanies the ores of iron in greater or less quantity, and frequently combines with the reduced metal.

There are several points which require nice adjustment in this process of reduction. The slag must not be of too fusible a description, otherwise the iron falls to the bottom before it has thoroughly combined with the carbon, and is not completely melted; a sufficiency of lime should always be present to neutralize the whole of the silica, for unless this be attended to a silicate of protoxide of iron is formed, and runs off in waste. Indeed, a small excess of lime is advantageous, as it removes sulphur, if present, in the shape of sulphide of calcium. At the same time the calcareous matter must not be too abundant, otherwise the working of the furnace is obstructed; the slags which are formed being of a less fusible character are but imperfectly melted, the iron is entangled within them, it is again partially oxidated by the blast, and the product of the furnace is greatly diminished. Experience has shown that the slags (which are chiefly composed of the mixed silicates of alumina and lime) are most fusible when the oxygen of the silica amounts to double that in the bases with which it is combined, and when the proportion of lime employed as a flux is such as would be furnished by adding 2 parts of limestone for every 3 of clay contained in the ore. A slag of this kind, however, can only advantageously be formed when the ore is smelted with charcoal, a fuel

which contains but little sulphur, and which allows the reduction to be effected at a comparatively moderate temperature. When coal or coke is used as the fuel, an excess of lime is required to carry off the sulphur introduced by the pyrites of the coal, and the slag which is produced under these circumstances is found to work most advantageously when the proportion of oxygen in the bases is nearly equal to that of the silica. The temperature of a blast-furnace fed with coal or coke is much higher than that of one in which charcoal is used. Slags containing several bases are more fusible than when one or two only are present, the different silicates aiding the fusibility of each other.

It is also necessary to proportion the supply of air rightly; if too much be thrown in, the furnace becomes unduly cooled; if too little, the supply of oxygen is insufficient for the maintenance of a proper temperature by a due amount of combustion. These, however, are points the successful regulation of which can only be acquired by experience.

The stream of air for the blast is not supplied in intermitting gusts, but is equalized as much as possible: where the cold blast is used, this object is attained by employing an air chamber or reservoir; and where the hot blast is employed, the long pipes required for heating the air answer the same purpose.

(626) *The Hot Blast.*—The mass of air which passes through one of these furnaces is enormous, being not less than 160,000 cubic feet, or about 6 tons weight, per hour. It is evident, therefore, that this immense volume of air must exercise an extraordinary cooling effect upon the contents of the furnace. This evil has been much reduced of late years by the introduction of air which has been previously heated. In this contrivance, which is known as the *hot blast*, the air, before it reaches the furnace, is made to pass through a series of pipes which are maintained at a high temperature, either by means of a separate furnace, or by a portion of the waste heat of the blast furnace itself: in the latter case the hot gases are conveyed through flues which pass from the upper part of the furnace into the chamber which contains the pipes; the necessary draught being maintained by a chimney furnished with a damper. A jet of the escaping blast should have a temperature sufficiently high to melt a strip of lead when held in it. The temperature of such a jet as it issues from the tuyère is somewhat higher than 600°. Mr. E. Cowper has improved upon this plan by burning the gases which escape from the furnace, in a chamber of brickwork filled with fire-bricks so arranged as to allow the heated gases to circulate freely around them. Two such

chambers are prepared; as soon as the bricks in one of these chambers are red hot, the current of gas from the furnace is cut off, and directed into the other chamber, in order to heat it. In the meantime a current of cold air is forced through the heated chamber, and a hot blast of from 1200° to 1300° is thus obtained. Each chamber is worked alternately; the one becoming heated whilst the other is employed in heating the blast. In this way nearly the whole of the heat of the waste gases may be economized.

The saving of fuel effected by the employment of the hot blast is immense, and is much greater than was at first anticipated: $2\frac{3}{4}$ tons of coal are now amply sufficient for the production of a ton of iron, from ore which would have required 8 tons when the cold blast was used. This saving is effected owing to the operation of several causes, one of which is, that raw coal may now be used in the furnace instead of coke: moreover, as a smaller quantity of fuel is required in the furnace to raise the injected air to the necessary temperature, so also a smaller quantity of air is needed to maintain the combustion: the maximum heat of the furnace is obtained lower down in the 'crucible,' so that the upper portions of the furnace do not become so intensely heated: the reduction of the ore consequently takes place nearer to the bottom, and the heat is thus concentrated and economized. In the year 1845, the hot blast was used in every furnace in Scotland, with the exception of one at the Carron Works, and it was computed that the change from the cold to the hot blast had effected a saving of coal in that country alone amounting to 2,000,000 tons annually. (*North Brit. Review*, No. vii., p. 128.) Even in a hot-blast furnace, however, the quantity of fuel which is wasted is enormous. Bunsen and Playfair, from their elaborate experiments at Alfreton, make the almost incredible estimate that somewhat more than $\frac{4}{5}$ths of the total quantity of heat producible from the fuel consumed is lost, owing to the escape of unburned combustible matter in the form of gases, such as carbonic oxide, carburetted hydrogen, and hydrogen, which are still fit for use. Since the publication of these researches, Mr. Budd and other iron-masters have economized a portion of the heat contained in the escaping gases, in heating the blast and in generating steam.

The iron obtained by the use of the hot blast is inferior in tenacity to cold-blast iron; a circumstance which appears to be partially due to the fact that the proportion of silicon is greater in hot- than in cold-blast iron; it is also to be noticed, that in the employment of the hot blast uncoked coal is used, a fuel which contains more sulphur, and probably also more phosphorus, than

coke, which is required in working with the cold blast. Crace Calvert has recently introduced a method of purifying the fuel, which enables him also to employ coal which, on account of the large proportion of pyrites which it contains, could not formerly be used for iron smelting. His process consists in mixing from 1 to 2½ per cent. of chloride of sodium with the coal previous to coking, the proportion of the salt being varied according to the quantity of pyrites present in the coal. He has also found, that if the same proportion of chloride of sodium be added to the raw coal, and the mixture be charged at once into the blast furnace, results are obtained almost equally satisfactory. The sulphur appears to be expelled in the form of chloride of sulphur.

A furnace in full work requires an hourly supply of rather more than 1½ tons of solid material, consisting on an average of 5 parts of coal, 5 of roasted ore, and 2 of limestone. The roasted clay-iron ore yields on an average 35 per cent. of iron, and each furnace when in full activity furnishes from 8 to 10 tons of metal in the 24 hours. Every morning and evening it requires to be tapped: on these occasions the iron is run into shallow grooves in the sand, and forms the cast iron, or pig iron of commerce. A good furnace, if well managed, may be made thus to work uninterruptedly without repair for many years.*

(627) *Varieties of Cast Iron.*—Cast iron differs greatly in quality; the differences observed in it depend in part upon differences in the proportion of carbon and silicon which it contains. The composition of these carbides varies considerably, within certain limits; but it does not appear that iron is capable of combining with more than about 5 per cent. of carbon. A compound of carbon having the composition of Fe_4C, or the *tetracarbide*, would consist of 94·92 of iron, and 5·08 of carbon; and this is very nearly the composition of the hardest and most fusible kind of white cast iron, which, from the circumstance of its crystallizing in flat brilliant tables, is termed by the Germans *spiegeleisen* (or mirror iron): according to Gurlt, the specific gravity of this carbide is 7·65. Faraday and Stodart found the most highly carburetted iron which

* The production of iron in Great Britain in 1858 amounted to about 3,456,000 tons. It was stated in 1855, by Mr. Blackwell, that the annual production of iron in different countries was then as follows:—

	Tons.		Tons.
England	3,000,000	Belgium	200,000
France	750,000	Russia	200,000
United States	750,000	Sweden	150,000
Prussia	300,000	Germany	100,000
Austria	250,000	Other States	300,000

In all, six millions of tons, of which Great Britain supplied one half.

they could produce, to consist of—iron, 94·36; carbon, 5·64. Gurlt (*Chem. Gaz.*, 1856, p. 231) has described another definite form of cast iron (Fe_8C), the *octocarbide*, which when pure contains 2·63 per cent. of carbon. It has a sp. gr. 7·75, is of an iron-grey colour, and has a hardness much inferior to that of the tetracarbide, being slightly malleable. It crystallizes in confused octohedral groups, and according to Gurlt is the principal constituent of grey cast iron. In many varieties of cast iron the carbon exists in two distinct forms,—one portion being chemically combined with the metal, the other being mechanically diffused through it in the condition of graphite, the scales of which may be distinctly seen with a magnifying lens, when the surface of a freshly fractured bar is examined. These scales remain unacted upon when the metal is dissolved in diluted acids; the combined carbon under such circumstances unites with hydrogen, and forms an oily-looking liquid of ill odour. In addition to carbon, cast iron also contains silicon, the proportion of which is equally liable to variation; the quantities of silicon which have been found in pig iron range between 3·5 and 0·25 per cent.*

The following table will serve to illustrate the general composition of some varieties of cast iron:—

	Gurlt.			Bodemann.		Abel.	
	Grey. Coal.	Mottled. Hot blast.	White. Gartsherrie.	Grey hot blast.	Mottled cold blast.	Grey French charcl.	White Silesian very crys.
Specific gravity . .	7·21	7·21	7·41	7·166	7·43	7·000	7·531
Carbon, combined .	1·021	1·793	2·457	1·44	2·78	...	4·94
Graphite	2·641	1·110	0·871	2·71	1·99	3·40	
Silicon	3·061	2·165	1·124	3·21	0·71	0·80	0·75
Sulphur	1·139	1·480	2·516	trace	trace	0·05	trace
Phosphorus . . .	0·928	1·171	0·913	1·22	1·23	0·45	0·12
Iron	90·236	89·314	89·863	91·42	93·29	95·18	88 57
Manganese	0·834	1·596	2·715	trace	trace	...	5·38
Copper	...	...	...	...	...	...	0·24
Arsenic	...	...	...	...	...	trace	
Cobalt	...	...	...	...	...	...	trace
Chromium	...	...	...	...	...	trace	
	99·860	98·629	100·459	100·00	100·00	99·88	100·00

Gurlt's specimens were all made in the same furnace, and with the same material; the grey at the highest temperature, the white at the lowest.

* Karsten found that when cast iron was melted with sulphur in a covered clay crucible, there was formed on cooling, a layer of sulphide of iron upon the surface, then a layer of graphite, and beneath this a layer of carbide of iron in the maximum degree of carburation. These effects may be thus explained:—Carbon is incapable of decomposing sulphide of iron, but sulphur can displace carbon from the carbide. On the addition of sulphur to the melted cast iron

The fusing point of cast iron varies with its composition; that of an average specimen was estimated by Daniell at 2786° F.

In commerce there are three principal varieties of *cast iron*, known respectively as Nos. 1, 2, and 3. No. 1 is called *grey* cast iron; No. 2, *mottled* cast iron; and No. 3, *white* cast iron. The first two are soft, and contain carbon disseminated in an uncombined form through the mass. Grey cast iron is soft; it may be filed, drilled, and turned in the lathe, and though somewhat less fusible than the white, is preferred for casting, since when melted its liquidity is more perfect. This variety is that which is generally produced from a furnace in good working order; if cooled suddenly, it is often converted into white cast iron. The fracture of the *mottled* variety is in large coarse grains, among which points of graphite are distinctly visible; it is very tough, and is valued for casting ordnance. It may be obtained for this purpose by partially refining good grey iron. *White* cast iron contains about the same amount of carbon as the mottled iron, but the whole of the carbon appears to be chemically combined with the metal. The white variety does not pass through a pasty condition as a preliminary to liquefaction; it is more fusible than either of the others, is lighter in colour, very hard and brittle, has a lamellar crystalline fracture, and a specific gravity varying between 7·2 and 7·6. It usually contains less silicon, but more sulphur and phosphorus than grey iron. White cast iron seems in some cases to owe its colour to the presence of manganese. A much higher temperature in the furnace, and consequently a greater consumption of fuel, is required for the production of grey than of white iron. This may probably arise from the fact, that if white iron be melted and exposed to a temperature considerably higher than its melting point, the tetracarbide of iron is decomposed, and if it be allowed to cool very gradually, a portion of the carbon crystallizes out as graphite, and grey cast iron is produced. In the process of casting heavy articles this carbon separates, and is thrown off in the form of brilliant scales, termed by the casters *kish*.

The peculiar value of iron castings depends upon its property of expanding at the moment of solidification. It thus furnishes

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the carbon gradually becomes concentrated in that part of the iron not combined with the sulphur, until its point of saturation with carbon is reached, and then the graphite is separated. According to the same authority, both phosphorus and silicon act in a similar manner, phosphide and silicide of iron being formed, whilst the carbon becomes concentrated in the remainder, until the excess of carbon is expelled and crystallizes in the form of graphite. When the proportion of phosphorus, of silicon, or of sulphur, is but small, the compounds which they form with the iron remain disseminated through the mass of cast iron, and exert an important influence upon its texture and tenacity.

an admirable material for taking the most minute impressions, as is well exemplified in the beautiful castings obtained from Berlin.

Small articles made of cast iron, such as key blocks, stirrup irons, &c., may be rendered malleable by packing them in powdered hæmatite, then heating them to redness for some hours, and allowing them to cool very slowly. In this case the oxygen of the oxide removes a portion both of the carbon and of the silicon, by a process of cementation the reverse of that which takes place during the manufacture of steel: the carbon is gradually removed from the outer layer of the metal, and is slowly transmitted from particle to particle through the solid bar, till it reaches the surface, where it undergoes oxidation at the expense of part of the oxygen of the hæmatite. The annexed analyses contain the results furnished by a sample of iron both before and after it had been thus treated. The cast iron was obtained from the Lancashire brown hæmatite:—

	Brittle.	Malleable.
Specific gravity	7·684	7·718
Iron (by loss)	95·732	98·711
Carbon { combined . .	2·217	0·434
Carbon { uncombined .	0·583	0·446
Silicon	0·951	0·409
Aluminum	trace	trace
Sulphur	0·015	
Phosphorus	trace	trace
Sand	0·502	
	100·000	100·000

(628) *Conversion of Cast Iron into Wrought Iron.*—1. *Refining.*—The pig iron as delivered from the furnace is, as already noticed, far from pure: it contains variable quantities of carbon, silicon, sulphur, and phosphorus, besides traces of other metals, such as aluminum, calcium, and potassium. Before it can be converted into the wrought iron of commerce, it has to undergo a process for the removal of these extraneous matters. Many castings may be made at once with pig iron, but it cannot be worked at the forge.

In order to effect the purification of the crude pig iron, it is necessary to expose it to the regulated action of oxygen at a high temperature, so as gradually to burn off these oxidizable substances, and leave the iron. The pig iron is usually first remelted in quantities of from 25 to 30 cwt., upon the hearth of a sort of forge,

termed the *finery* or *refinery*, the fire of which is animated by a double row of blast pipes. During this operation, which lasts about two hours, the metal loses from 10 to 12 per cent. of its weight. The silicon is more readily oxidized than the carbon, so that it is the impurity which is first attacked in the refining process, but at the same time a small portion of the carbon contained in the iron is burned off as carbonic oxide; part of the iron also becomes converted into the protoxide, which unites with the silica furnished by the oxidation of the silicon, and with the sand which adhered to the surface of the cast metal: a fusible slag consisting of a highly basic silicate of protoxide of iron ($2\ FeO,SiO_2$) is thus produced. The excess of oxide of iron in this slag again reacts upon the melted metal, and by imparting a portion of its oxygen to the silicon and carbon disseminated through the mass, burns off an additional quantity of these substances; portions of sulphur and phosphorus are also separated by oxidation in this process, and accumulate in the slag. The melted iron is then run off and formed into a flat cake, 2 or 3 inches thick, and as soon as it begins to solidify it is suddenly cooled by pouring water upon it; a hard, white, brittle mass is thus obtained, which is broken up into fragments. In this operation coke is the combustible generally made use of, but where iron of superior quality is required, as in making tin-plate, charcoal is employed. Ordinary coke contains sulphur and earthy impurities which injure the quality of the iron.

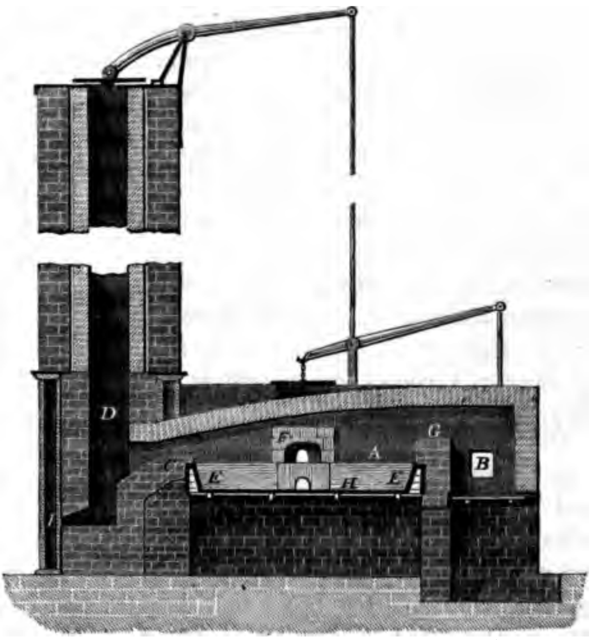
The effect of the operation is well exhibited by the following analysis quoted by Regnault, giving the composition of a portion of cast iron before refining, and a portion of the same metal after it had passed through the refinery furnace.

	Before refining.	After refining.
Carbon	3·0	1·7
Silicon	4·5	0·5
Phosphorus	0·2	
Iron	92·3	97·8
	100·0	100·0

(629) *Puddling.*—The refined metal still retains a considerable proportion of carbon and some silicon. In order to remove them it is next introduced, in charges of from 4 to 5 cwt., into the *puddling furnace*. This consists of a reverberatory furnace, connected with a chimney of 40 or 50 feet in height, and capable of producing a powerful draught, which is under complete command

by means of a damper. Fig. 327, represents a section of the puddling furnace; A, is the bed, or hearth, upon which the iron for puddling is placed; B, is the fire-place with the aperture for

FIG. 327.



stoking, which is closed with coal, and not by a door as usual in most furnaces: G is the bridge which separates the fuel from the metal: the hearth, A, is lined with cast-iron plates, E E, which are prevented from melting by the free circulation of air beneath them; C is the flue leading to the chimney, D, at the top of which the damper is shown; H is the plate upon which the iron rests during the puddling process; it is protected from the heat by a coating of powdered hæmatite, of sand, or of slag;* F is the working door of the furnace, and I is the *flosshole*, or aperture through which the slags are removed from the hearth.

For the coarser kinds of iron the furnace is sometimes charged partially, or even wholly, with iron that has not been refined. Iron which has undergone the refining process never becomes so completely liquid in puddling as when crude pig iron is employed, but the product is a metal of finer quality.

* The employment of lime as a lining to the furnace has been recommended; it is said to improve the quality of the iron by removing sulphur more completely, and at the same time to diminish the rate of oxidation.

Supposing the crude pig iron to be used, the pigs slowly become melted, and the metal when first heated forms a thick pasty mass, which gradually becomes fluid and at length perfectly liquid. At this stage the metal is violently agitated, and assumes an appearance of boiling, owing to the escape of the carbonic oxide in jets, which take fire and burn with a blue flame, whilst the melted mass swells up to several times its original bulk. It is now briskly stirred by the puddler to promote oxidation.

When *refined* iron is used it is often mixed with a certain proportion of scales of oxide from the forge, and is then gradually brought into complete fusion, carefully avoiding the contact of fuel. The mass is well stirred, so as to incorporate the oxide of iron with the melted metal; oxygen is transferred from the oxide thus introduced, to the carbon of the melted iron, and carbonic oxide is formed abundantly; but the appearance of boiling is less marked than when crude pig iron is used. In either case, the metal by degrees becomes less fusible as the carbon diminishes in quantity, and at length it is converted into a granular, sandy mass. The heat is now raised till it becomes very intense, and air is carefully excluded by closing the damper and doors. The metal again begins to soften and agglomerate. The puddler gradually collects it into balls or *blooms* upon the end of an iron rod; he then removes it from the furnace in masses weighing about three-quarters of a hundredweight, and subjects it, whilst still intensely hot, to the action either of a massive hammer, or a powerful press, called the *shingling press.* The melted slag is thus forcibly squeezed out, the particles of metal are brought nearer together, and the density is increased. The iron is then fashioned into a bar by passing it between grooved rollers, and the bar thus obtained is cut into lengths, then piled up in a reverberatory furnace and re-heated; it is again rolled, doubled upon itself, and re-heated and rolled. Upon the best qualities of iron this process is repeated several times, in order to render its fibres parallel to each other, by which the toughness of the metal is much increased. The iron is now nearly pure; it contains from $\frac{1}{400}$th to $\frac{1}{200}$th of its weight of carbon, and about $\frac{1}{500}$th of silicon. The presence even of this small proportion of carbon adds materially to the toughness and hardness of the metal. The process of puddling occupies about two hours; and provided it has been properly refined previously, the metal loses from 7 to 10 per cent. of its weight.*

* Calvert and Johnson (*Phil. Mag.*, Sept. 1857) have made a series of analyses of the iron in different stages of the process of *boiling*. They em-

The slag produced during the operations of puddling and refining consists chiefly of a basic silicate of the protoxide of iron, and contains upwards of 60 per cent. of the metal. This slag or *finery cinder* is reduced in the blast furnace in the same manner as the original ore, but it is always found to produce a defective iron, technically known as *cold short*. Such iron may be forged well at a red heat, but when cold it is brittle and rotten. This defect is attributed to the presence of phosphorus, which is separated from the crude metal in the form of phosphate of iron during the puddling. When the slag is reduced in the blast furnace, both the phosphorus and the iron are deprived of their oxygen, and by their union, as phosphide of iron, form the faulty metal in question.

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ployed in their experiments good cold-blast Staffordshire grey iron, No. 3, such as is used for making iron wire.

	Time after charging.	Carbon.	Silicon.	Phosphorus.	Sulphur.
Pig iron		2·275	2·720	0·645	0·301
1st sample	40′	2·726	0·915		
2nd „	60′	2·905	0·197		
3rd „	65′	2·444	0·194		
4th „	80′	2·305	0·182		
5th „	95′	1·647	0·183		
6th „	100′	1·206	0·163		
7th „	105′	0·963	0·163		
8th „	110′	0·772	0·168		
9 Puddled bar		0·296	0·120	0·139	0·134
10 Wire iron		0·111	0·088	0·117	0·094

A charge of 2 cwt. of iron was introduced into the bed of the furnace, without any addition of oxide of iron: in 40 minutes it became fused, and on cooling the sample suddenly, it yielded a brittle mass like white iron. It will be seen that whilst the carbon increases during the first stage of the process, the silicon undergoes a very rapid diminution. The 3rd sample was taken just before the beginning of the *boil*, when the iron was in its most fluid condition. No. 4 was taken during the full boil, and consisted of small detached brittle granules surrounded by slag. No. 5, the boil was completed. It was still in granules, but they were slightly malleable. No. 6, the iron was collecting into masses. No. 7 was taken during balling, and in No. 8 the balls were just ready for the shingling press. The 'puddled bar' was taken from the iron after it had been hammered; and the 'wire iron' was the same after it had been broken up into billets, reheated, and rolled preliminary to drawing.

The slag which was separated during the operation was found to have the following composition:—

Silica	16·53
Protoxide of iron	66·23
Sulphide of iron	6·80
Phosphoric acid	3·80
Protoxide of manganese	4·90
Alumina	1·04
Lime	0·70
	100·00

Mr. Bessemer has attempted to substitute for the processes of puddling and refining a method of purification which consists in forcing cold air at a pressure of 10 or 12 lb. upon the square inch through melted cast iron, which, as it runs from the furnace, is received into a cylindrical vessel covered with an arched head and lined with fireclay, the air being driven in at the bottom, through several tuyères. An intense combustion occurs, attended with remarkable elevation of temperature, owing partly to the oxidation of the iron, and partly to that of the carbon; the latter, being converted into carbonic oxide, escapes at all points of the mass, throwing the whole into violent agitation, which subsides as soon as the carbon is burnt off; when this occurs the melted iron nearly freed from carbon is run off into moulds. A great loss of iron is, however, incurred in this operation; a copious slag of oxide of iron, mixed with a little silicate, is produced, and in this a large quantity of metallic iron is entangled: not less than 20 per cent. of the metal is thus wasted, and the malleable iron still retains nearly all the phosphorus and much of the sulphur originally present.

But though the process of Bessemer has not been attended with the important results which were anticipated from its employment in refining the ordinary pig iron obtained by the smelting of clay iron-stone with coal, it is stated to have been eminently successful when applied to the pure Swedish charcoal pig iron, which has by its means been converted by a single operation of short duration into cast steel of the finest quality.

(630) *Production of Wrought Iron direct from the Ore.*—The pure ores, which consist of magnetic oxide, or of peroxide of iron, are frequently converted at once into wrought iron, without the production of cast iron. This process is practised in the Pyrenees, by what is termed the Catalan forge, and still more largely in the *bloomery forges* of the United States. In the American bloomery forge either the hot or the cold blast may be employed:—The ore having been first reduced by stampers to a coarse powder, is placed on the top of the coal in the forge which has been kindled for its reception; a high heap of coal is kept on the fire, and a gradual supply of ore is maintained: as the metal is reduced, it sinks to the bottom in a pasty state; when sufficient has been added to form a bloom, or ball, the metal is collected on an iron bar, heated before the blast-pipe, and then hammered, rolled, and welded, as if it had come from the puddling furnace (Overman's *Metallurgy*, p. 544). This method yields a very pure iron when

charcoal is employed, but the consumption of fuel per ton of metal is much greater than in the blast furnace; a large portion of the ore is also wasted in the form of slags, which are very rich in oxide of iron. The iron produced by this process frequently contains sufficient carbon to give to it some of the properties of steel: for instance, it becomes much harder when heated and suddenly cooled. Iron of this description is valuable in the manufacture of plough-shares, and heavy articles requiring both toughness and hardness.

(631) *Manufacture of Steel.*—Iron, when combined with a smaller proportion of carbon than is contained in cast iron, furnishes the valuable compound well known as *steel*, of which there are several varieties. The quantity of carbon in good steel varies between 0·7 and 1·7 per cent.; but steel which possesses the greatest tenacity has been found to contain from 1·3 to 1·5 per cent. of carbon, and about 0·1 of silicon. *Natural steel* is produced directly from the best cast iron by heating it by means of charcoal on the refining hearth, as in the operation which precedes the process of puddling; the oxygen burns off a portion of the carbon from the cast iron, and steel is left. In some of the Welsh iron works steel is now made upon the bed of the puddling furnace itself, by carefully arresting the operation at a stage short of the complete oxidation of the carbon. The preparation of natural steel is, therefore, an intermediate stage in the conversion of cast into wrought iron. Iron which contains manganese is best fitted for the preparation of this kind of steel. The mass thus obtained is rendered homogeneous by forging. It yields a steel of inferior quality, which is employed for making agricultural implements and springs for machinery.

For more delicate purposes *blistered steel* is made use of: this is obtained by means of *cementation*, which is an operation just the reverse of that by which natural steel is formed. This process is carried on in a furnace into which two rectangular boxes of brickwork or stoneware, for the reception of the bars of iron which are to be converted into steel, are built; the fire-grate is between these boxes, around which the flame circulates freely. This conversion is effected by heating the iron in contact with powdered charcoal, or with soot; the carbonaceous matter in either case is usually mixed with about a tenth of its weight of common salt and wood ashes, forming what is technically termed *cement powder*. In preparing a charge, the bottom of each box is covered with a layer of the cement powder to the depth of about an inch, and upon this

at intervals of about half an inch, a layer of bars of the best malleable iron is placed, resting upon their edges. The interstices between the bars are also filled with cement powder, which is tightly packed around the iron; above this is a layer of the powder, then another layer of bars, and so on in succession until the box is nearly full, when it contains from 5 to 6 tons of iron. The remaining space is now covered with a layer of damp sand of from 3 to 6 inches in depth, and the fire is gradually raised to a full red heat, or to about the temperature required for melting copper; at this point it is steadily maintained. One of the bars of steel is so placed that it can be removed from time to time during the operation, for the purpose of ascertaining the process of the carburation by inspection. The process is usually complete in six or eight days; but the time required necessarily varies with the thickness of the iron bars operated on; the fire is then gradually reduced, and the furnace is suffered to cool slowly, an operation which lasts ten days or a fortnight. The steel thus obtained retains the form of the iron, but it is covered with blebs or blisters, by which the surface is rendered irregular and uneven. The mass is found to have been penetrated by carbon which has been transferred from particle to particle of the metal, the properties of which it has completely changed. It has been supposed that these blisters may possibly arise from the combination of parts of the carbon with oxygen derived from particles of oxide of iron, which are apt to be mechanically retained even in the most carefully prepared bars. Carbonic oxide would thus be produced, and imprisoned in the tenacious metal, which in its softened state would be raised by it into bubbles or blebs. Great care, however, is generally taken to exclude slag and oxide of iron from bars which it is intended to convert into steel: in the majority of instances it is more probable that the blisters are occasioned by the combination of carbon with the sulphur which is still retained by the iron, and which, by forming the volatile bisulphide of carbon, would produce the effect (T. H. Henry). All bar iron contains traces of sulphur; but in steel sulphur is never present, and there appears to be no other mode of accounting for its uniform absence than its removal during the process of carburation in the form of bisulphide of carbon.

By the process of cementation the iron has been combined with about 1·5 per cent. of carbon: it is now much more fusible than before. It has also entirely lost its fibrous texture; and when broken across exhibits a close, fine-grained fracture. Steel may also be made without direct contact with carbon, by simply

heating the bars in carburetted hydrogen; but this process has not come into general use.

Blistered steel is never homogeneous, the surface being always more highly carburetted than the inner portions of the bars. This variety of steel is employed for files, tools, and hardware of all descriptions. When blistered steel is fused it forms *cast steel*, which, from being more uniform in texture, is of superior quality, as the carbon is more equally distributed throughout the mass: it is employed for cutlery of the best description. *Tilted steel* is also obtained from blistered steel; it is first broken up into lengths of about 18 inches, then bound into fagots and raised to a welding heat in a wind furnace, where it is covered with sand, which combines with the superficial coating of oxide of iron and forms a fusible slag: the red-hot fagot is then rolled, and forged, by means of the tilt-hammer, into smaller bars. All steel is improved by this process of hammering. These tilted bars, when broken up and welded together, form *shear steel*.

For many purposes the addition of a small quantity of manganese is an improvement to the quality of the steel. If about 1 per cent. of carbide of manganese, or of a mixture of charcoal and oxide of manganese, be introduced into the melting-pot, a steel is obtained of fine, close grain, which admits of being welded to wrought iron; a property not possessed by ordinary steel. The experiments of Faraday and Stodart led them to the conclusion that the addition of small quantities of silver, of chromium, or of rhodium, to good steel, furnished a steel of a superior kind. The combination of 8 or 9 per cent. of tungsten with ordinary steel is said to yield a material remarkable for hardness and elasticity, which increases its value for certain purposes. When steel is to be used for the manufacture of dies for coining, the presence of a small proportion of phosphorus is beneficial (Brande).

When diluted nitric acid falls upon steel, a dark grey spot is produced, owing to the solution of the metal in the acid whilst its carbon remains unacted upon: the acid produces a green spot upon iron. The acid acts unequally upon different parts of the surface in certain of the finer varieties of steel, and thus produces a veined appearance, such as was formerly given to the celebrated Damascus blades. The Damascus steel is more highly carburetted than ordinary steel, and if allowed to cool slowly, it separates into layers of two different degrees of carburation (Bréant); hence certain parts, when acted on by diluted acid, leave more carbon than others; the form and direction of these veins vary with the mode of forging adopted.

Wootz is a finely damasked, hard cast steel, of excellent quality, which is obtained from India. Faraday found aluminum in a sample of this steel which he analysed, and was disposed to refer its peculiar qualities to the presence of this metal. It appears, however, from the experiments of Henry (*Phil. Mag.*, July, 1852), that aluminum is not always present in wootz. He gives the following as the composition of a bar of genuine Indian wootz, of specific gravity 7·727:—

Carbon { combined	1·340
Carbon { uncombined	0·312
Silicon	0·042
Sulphur	0·170
Arsenic	0·036
Iron	98·100
	100·000

Other analysts have also failed in finding aluminum in wootz.

The physical properties of steel differ materially from those of iron. As already mentioned, steel is granular in texture, brittle, and more easily melted than iron. Its most characteristic property, however, consists in its power of assuming a hardness scarcely inferior to that of the diamond when heated to redness and then suddenly cooled by plunging it into water, mercury, or oil. After this treatment it is rendered extremely brittle, and almost perfectly elastic. It can then no longer be attacked by the file.

This extreme hardness and brittleness may be removed by the process of *tempering*, which is a peculiar mode of annealing; it consists in heating the steel moderately and then allowing it to cool. The tempering of steel is an operation of great practical importance, as from the variety of purposes to which steel is applied, it is required of very different degrees of hardness, and upon the due adjustment of this quality much of its utility depends. The degree to which the temperature is raised in the second heating regulates this point: the higher the heat the softer is the steel. In practice the workman judges with sufficient accuracy of the temperature to which the metal has been exposed, by observing the colour which the steel assumes owing to the varying thickness of the film of oxide which is formed upon its surface. It is easy to show that this colour is due to the formation of a film of oxide; for by painting on the surface of the steel various devices in oil or varnish, and then exposing it to heat, the surface of the blade becomes coloured in every part excepting those portions which have been varnished, and these, when the varnish is removed, retain their original polish. The first perceptible tint is a light straw colour, which is produced by the lowest degree of heat, and

indicates the hardest temper; the heat required is from 430° to 450°; it is used for lancets, razors, and surgical instruments: at 470° a full yellow is produced; it is the temper fitted for scalpels, pen-knives, and fine cutlery. The temperature of 490° gives a brown-yellow, which is the temper for shears intended for cutting iron. At 510° the first tinge of purple shows itself: this is the temper employed for pocket-knives: 520° gives a purple, which is the tint for table and carving-knives. A temperature from 530° to 570° produces various shades of blue, such as are used for watch-springs, sword-blades, saws, and instruments requiring great elasticity (Stodart). The different degrees of heat may be exactly regulated by heating the different articles in a fusible metal or oil-bath, the temperature of which is ascertained by means of thermometers, though in ordinary cases this degree of nicety is not observed.

Hardened steel is somewhat less dense than wrought steel. It appears that a portion of the carbon contained in steel, before the alloy has been hardened, is in the uncombined state; this portion is left in the form of graphitic scales, when the metal is dissolved in hydrochloric acid: but after the steel has been hardened, the whole of the carbon is chemically united with the iron; and when treated with acids, is left in the form of a liquid hydrocarbon. Before it has been hardened it may be worked as easily as iron, and in certain cases may be welded upon that metal. Instruments are completely finished in the soft state, and are then hardened and subsequently tempered.

It is sometimes desirable to convert articles manufactured from soft iron superficially into steel. This is termed *case-hardening*, and is effected by heating them in contact with powdered cast-iron turnings, or sometimes with powdered charcoal. The same object is attained if they are sprinkled when red-hot with powdered ferrocyanide of potassium.

(632) *Preparation of pure Iron.*—In order to obtain iron chemically pure, Berzelius recommends that filings of the best bar iron be intimately mixed with one fifth of their weight of pure peroxide of iron, and placed in a Hessian crucible, covered with pounded glass (free from lead); the cover is then to be carefully luted on, and the crucible to be exposed for an hour to the strongest heat of a smith's forge. By this means all traces of carbon and of silicon are oxidized at the expense of the oxygen of the peroxide of iron, whilst the excess of oxide forms a fusible slag with the glass. If the operation be successful, the iron will be melted into a button, with a lustre approaching that of silver,

Such iron is very tough, and much softer than ordinary bar iron it has a sp. gr. of 7·8439. Pure iron may also be obtained in the state of fine powder, by decomposing the pure peroxide at a red heat in a current of hydrogen gas.

(633) *Properties of Bar Iron.*—The bar iron of commerce is never pure. It always retains small quantities of carbon, varying from 0·2 to 0·4 per cent., and traces of silicon and sulphur; occasionally, also of phosphorus and arsenic. The presence of this small quantity of carbon much increases its hardness and tenacity, but the other ingredients act injuriously upon the metal.

Bar iron has a bluish-white or grey colour, and is endowed with considerable lustre and hardness; it takes a high polish: its texture is usually fibrous, and when broken across, it exhibits a ragged or hackly fracture; when rubbed, it emits a peculiar characteristic odour. The average specific gravity of good bar iron is 7·7. It requires the most intense heat of a wind furnace for its fusion. Iron passes through a soft pasty condition before it is completely melted; this property is one of great practical importance: if two pieces of iron be heated to whiteness, sprinkled with sand, and hammered together, they may be united or *welded* so completely that the junction is as tough as any other part of the metal. The sand is used as a flux to the oxide of iron, with which it forms a slag, which coats each piece of the metal; by the blow of the hammer this layer of melted matter is forced out, and the two clean surfaces of metal become united together. At a red heat iron may be forged into any shape with facility, but at ordinary temperatures it possesses but little malleability, as compared with gold and silver. It however admits of being rolled into very thin sheets. In ductility, iron stands very high in the scale, and in tenacity it far exceeds all other known substances, with the exception of cobalt and nickel.

If compared with other metals, iron is inferior to many of them as a conductor of heat and of electricity. Its susceptibility to magnetism is peculiar; no metal exhibiting this property in any marked degree, excepting cobalt and nickel, and in them the power is developed to a much smaller extent. But though iron in its pure state is susceptible of magnetic induction, it cannot be permanently magnetized unless it be combined with carbon, as in steel; with oxygen, as in the loadstone (Fe_3O_4); or with sulphur, as in certain varieties of pyrites (Fe_3S_4), and (Fe_7S_8). It is especially worthy of observation, that if oxygen or sulphur be present in quantity either greater or less than in these particular compounds, not only is the power of retaining magnetism destroyed,

but the mass becomes almost indifferent to the action of a magnet. Iron loses its magnetic power when heated to redness, but recovers it again on cooling.

At a high temperature iron burns readily, emitting vivid scintillations, as may be seen at the blacksmith's forge, or still more brilliantly when a glowing wire is introduced into a jar of oxygen. The metal, however, preserves its lustre unchanged in dry air at ordinary temperatures, but when exposed to a moist atmosphere, its surface is quickly altered, and it becomes covered with rust. When once a spot of rust begins to show itself, the oxidation proceeds rapidly; moisture is absorbed from the air by the oxide, and thus a species of voltaic action is produced, the oxide performing the part of an electro-negative element, whilst the iron becomes electro-positive, and the atmospheric moisture acts as the exciting liquid. The carbonic acid of the air contributes in an important way towards increasing the rapidity with which this change occurs; but it is not indispensable. It appears that usually hydrated protocarbonate of iron is first formed, and is afterwards decomposed by the further absorption of oxygen, by which it is converted into the hydrated oxide, or rust of iron, whilst the liberated carbonic acid forms a fresh portion of protocarbonate: a portion of water is deoxidized in the process, and hydrogen is evolved; if a considerable heap of iron turnings be moistened and exposed to air, the peculiar odour of hydrogen, as evolved from a metallic carbide, is perceived, and the temperature of the mass rises considerably. Iron rust always contains ammonia, derived from the reaction of the hydrogen of the water upon the nitrogen of the atmosphere, which is dissolved in the water with which the metal is moistened. Even the native oxides of iron invariably contain traces of ammonia (Chevallier). Iron may be kept for any length of time without undergoing any change in water quite free from air, as well as in water containing a little free alkali. In a very finely divided state, such as that produced by reducing precipitated oxide of iron at a low temperature in a current of hydrogen gas, the metal takes fire by mere exposure to the atmosphere. If a small quantity of alumina be precipitated with the oxide of iron, so as to interpose some foreign matter between the particles of the metal, this pyrophoric property is much increased. At a red heat iron decomposes water rapidly, and liberates hydrogen (293), whilst the iron is converted into minute crystals of the black or magnetic oxide; the following equation illustrates the chemical change: $4\ HO + 3\ Fe = 4\ H + (FeO, Fe_2O_3)$.

Chlorine, bromine, and iodine combine quickly with iron, and

dissolve it easily at ordinary temperatures, if the metal be digested with them in water. Iron is soluble in diluted sulphuric and hydrochloric acids, with extrication of hydrogen. Even carbonic acid, when contained in water from which air is excluded, slowly dissolves this metal with extrication of hydrogen, and the carbonate of iron is dissolved in the excess of carbonic acid. Concentrated sulphuric acid has very little action on iron, even when boiled upon it,—a slow solution, attended with evolution of sulphurous acid, occurring: but the metal is rapidly attacked by nitric acid, with abundant evolution of binoxide of nitrogen.

(634) *Passive Condition of Iron.*—Under certain circumstances iron may be kept in concentrated nitric acid for weeks, without the slightest action, or alteration of the polish of its surface. There are various methods of producing this *passive condition* of iron in an acid of a moderate degree of concentration; some of these seem to indicate an intimate connexion with its voltaic relations. This will be rendered evident from the following statement of some of the circumstances under which this remarkable phenomenon is manifested. If a piece of clean iron wire be introduced into nitric acid, of a sp. gr. of about 1·35, immediate and brisk action ensues; but if the metal be touched beneath the surface of the liquid with a piece of gold, of platinum, or of plumbago, the chemical action, contrary to what might have been anticipated, is suddenly arrested if the temperature of the acid has not been allowed to rise too high. If a second iron wire be made to touch the first, and then be introduced into the acid, it also is rendered inactive. This second wire may be used in like manner to render a third inactive. But if any of these inactive wires be withdrawn from the acid, and exposed to the air for a few seconds, it will be found to be rapidly acted on upon again introducing it into the acid. If whilst in the acid the iron wire be made the zincode of a voltaic arrangement, oxygen gas is evolved from the surface of the iron, but does not combine with it. If, on the contrary, a piece of passive iron be made the platinode or negative plate of the arrangement, it is immediately attacked by the acid.

By heating the end of a clean iron wire in the flame of a spirit lamp so as to give it a superficial coating of oxide, the wire is brought into the passive condition.* If into acid containing a

* Similar effects are produced with wires of cobalt or of nickel, though with them the action is less strongly marked (Nicklès). Such wires, if placed in voltaic relation with an active wire of the same metal, are found to be strongly electro-negative towards it; but passive iron, cobalt, and nickel are electro-positive in relation to platinum. Andrews has shown that bismuth also may be rendered passive in concentrated nitric acid.

passive wire, a second ordinary wire, not in contact with the first, be introduced, brisk action on the ordinary wire ensues; and on causing the passive wire to touch the active one, immediate action occurs on both.

Strong nitric acid, of sp. gr. 1·45, renders all iron passive; the metal may be kept in it for years without losing its brilliancy, or showing any action; and a wire withdrawn from the strong acid, and plunged into acid of 1·35, still remains passive. If it be wiped first, and then plunged into the weaker acid, it immediately begins to be dissolved. If the acid be diluted below a density of 1·35, it rapidly dissolves the metal, whatever may have been its previous condition.

(634 *a*) *Alloys of Iron.*—Iron forms alloys with most of the metals; but they are not in general of much importance. The presence of small quantities of copper, of arsenic, or of sulphur, in iron, is said to occasion a defective quality of metal, technically known as *red short*. Such iron is tough at ordinary temperatures, but becomes brittle when heated to redness for forging.

The mode of preparing zinc-plate, or galvanized iron, has been already described (591). Tin-plate is prepared by an analogous process; it consists of iron superficially alloyed with tin.

(635) OXIDES OF IRON.—Iron yields four definite compounds with oxygen: 1. The *protoxide* (FeO), which is the basis of the green, or ferrous salts of iron: 2. The *sesquioxide* (Fe_2O_3), which is the base of the red, or ferric salts: 3. The black, or *magnetic oxide*, which may be viewed as a compound of the two preceding oxides (Fe_3O_4) or (FeO, Fe_2O_3); it does not form any definite salts: 4. *Ferric acid* (FeO_3), which is a weak and unstable metallic acid, and as such combines with the alkalies.

Protoxide of Iron; Ferrous Oxide ($FeO = 36$).—It is obtained in the form of a white hydrate by dissolving a pure protosalt of iron in water recently boiled, and precipitating by an alkali, the solution of which has been similarly treated, both being allowed to cool out of contact with air, and being mixed in vessels from which air is excluded. If this precipitate be boiled in a vessel from which oxygen is excluded, it loses its water of hydration, like the oxide of copper under similar circumstances. The hydrated oxide absorbs oxygen greedily from the air, passing through various shades of light green, bluish green, and black, till finally it assumes an ochry hue, due to the formation of the hydrated sesquioxide. It is insoluble in water, but is somewhat soluble in ammonia; this solution quickly absorbs oxygen from the air, and a film of insoluble sesquioxide of iron is formed upon its surface. The prot-

oxide is readily dissolved by acids, and forms with them salts which are known as the *protosalts of iron;* they have a green colour, and an astringent, inky taste. The solutions of these salts, when exposed to the air, absorb oxygen, and are decomposed; in which case salts of the sesquioxide are formed, one portion of which is retained in solution, whilst a basic salt of the sesquioxide falls as a rusty insoluble precipitate. For example, in the case of the protosulphate of iron, 8 atoms of the salt absorb 4 atoms of oxygen, and are decomposed as follows:—

$$\overbrace{10(FeO,SO_3)}^{\text{Protosulph. Iron.}}+5O+3HO=3\overbrace{(Fe_2O_3,3SO_3)}^{\text{Soluble Persulph.}}+\overbrace{(2Fe_2O_3,SO_3+3'Aq)}^{\text{Basic insoluble salt.}}$$

(636) *Peroxide, Red Oxide,* or *Sesquioxide of Iron; Ferric Oxide* ($Fe_2O_3=80$).—The anhydrous sesquioxide is obtained for the arts by igniting the protosulphate of iron (643), and is known under the names of *colcothar, crocus of Mars,* or *rouge,* according to the degree of levigation to which it has been submitted; it is extensively employed, amongst other uses, for polishing glass, and by jewellers for putting a finish to their goods. It is also employed as a red pigment.

The sesquioxide occurs native in great abundance: several of its varieties have been already mentioned as among the most valuable ores of iron; it contains 70 per cent. of the metal, and 30 of oxygen. The specular ore of Elba (sp. gr. 5·22) often presents natural facets of the most perfect polish, and of remarkable size and lustre. It occurs in forms of the rhombohedral system, and is isomorphous with alumina in corundum. Red hæmatite, or bloodstone (sp. gr. from 4·8 to 5·0), another of its varieties, is extremely hard, and, when polished, is employed for burnishing gilt trinkets.

Hydrates of Sesquioxide of Iron.—There are several of these. Brown hæmatite is the hydrate ($2\,Fe_2O_3, 3\,HO$) *Sp. Gr.* 3·98. This mineral is readily dissolved by acids. It contains 59·89 per cent. of iron, with 25·67 of oxygen, and 14·44 of water. Another native hydrate (HO, Fe_2O_3) has been found crystallized in cubes; it is isomorphous with the magnetic oxide of iron (FeO, Fe_2O_3), to which it corresponds in composition, 1 atom of protoxide of iron being displaced by 1 of water. Brown hæmatite gives the red and yellow colour to the different varieties of clay.

The sesquioxide is best obtained in a state of purity, by precipitating the sesquichloride of iron by ammonia in excess. It falls as a bulky light-brown flocculent hydrate, which shrinks remarkably as it dries: if precipitated in a cold solution, and dried

without heat over sulphuric acid, it contains $2\ Fe_2O_3, 3\ HO$ (St. Gilles), but it is apt to retain a little ammonia, which is easily expelled by heat. The same hydrate is also formed when moist iron is allowed to become oxidized by exposure to air. If dried at 212° it retains 10·11 per cent. of water, corresponding in composition to (Fe_2O_3,HO): but if the hydrate be not dried, but allowed to remain for some months under water, it becomes crystalline, and, according to Wittstein, is converted into an allotropic hydrate ($2\ Fe_2O_3, 3\ HO$). Hydrated peroxide of iron slowly parts with its water at a prolonged heat of 600°, and if subsequently heated to dull redness, it suddenly contracts in bulk, and glows brightly for a few moments whilst undergoing molecular change; after this it is dissolved by acids with difficulty, but is readily attacked by a solution of protochloride of iron in hydrochloric acid: at a very high temperature the sesquioxide loses one ninth of its oxygen, and is converted into the magnetic oxide of iron.

Hydrated sesquioxide of iron, when recently precipitated from cold solutions, is easily soluble in acids, forming the persalts of iron, or ferric salts; they have a strongly acid reaction, and do not crystallize: many of them are deliquescent. Their concentrated solutions have the property of dissolving a considerable excess of the oxide, in which case they assume a deep red colour. If these basic solutions be diluted and boiled, the peroxide of iron is entirely separated in the form of an insoluble subsalt. If well washed and freshly precipitated hydrated oxide of iron, obtained by the action of ammonia upon the sesquichloride in the cold, be boiled in water for 8 or 10 hours, its colour becomes changed from ochry brown to brick red, and it is converted into an allotropic modification of the hydrate (Fe_2O_3,HO), and by prolonged boiling a portion of it even loses all its water. It is insoluble in strong boiling nitric acid, and only slowly soluble in hot hydrochloric acid. Cold acetic acid, and cold diluted hydrochloric and nitric acids dissolve it, forming a red liquid which appears to be turbid by reflected light; concentrated nitric or hydrochloric acid occasions a red precipitate in this solution, but it becomes redissolved on the addition of water. The solution is also precipitated by the addition of any sulphate, or of any salts of the alkalies. If the ordinary hydrated sesquioxide of iron be kept long in water, especially if at the same time it be exposed to a low temperature, it experiences a similar modification in composition and properties. An acetic solution of this oxide, if kept for some time in a closed vessel at 212°, becomes of a brighter red colour. It appears to be turbid when viewed by reflected light, but clear by transmitted

light. It has lost its astringent metallic taste. The addition of a soluble sulphate causes an immediate precipitate, and so do the strong acids: it is no longer reddened by the addition of a sulpho-cyanide, and does not give a precipitate of Prussian blue with ferrocyanide of potassium (Péan de St. Gilles, *Ann. de Chimie*, III. xlvi. 47).

Hydrated sesquioxide of iron is now used to some extent for the purpose of purifying coal gas from sulphuretted hydrogen, which is always produced during the distillation of coal. For this purpose the oxide is mixed with sawdust, and placed in layers, of 10 or 12 inches in thickness, upon the perforated shelves of a dry lime purifier (1314): hydrated sesquisulphide of iron and water are formed; $Fe_2O_3, x\,HO + 3\,HS = 2\,Fe_2S_3, x\,HO + 3\,HO$. After the mixture has ceased to absorb any more sulphuretted hydrogen, it is oxidized by exposure to a current of air; hydrated sesquioxide of iron is thus reproduced, and sulphur is set free; $Fe_2S_3, x\,HO + 3\,O = Fe_2O_3, x\,HO + 3\,S$. The mixture may again be used for the same purpose as at first, and this process may be repeated several times in succession, until the accumulation of sulphur mechanically impairs the absorbent powers of the mixture. Considerable elevation of temperature attends the act of reoxidation, which must therefore be prevented from taking place with too much rapidity.

Sesquioxide of iron combines with some of the more powerful bases, towards which it acts the part of a feeble acid. The compounds which it forms by heating it with potash and soda are easily decomposed by water, but the oxide retains traces of these bases with great obstinacy. According to Pelouze, when 4 atoms of lime and 1 atom of peroxide of iron are precipitated together and boiled, they unite and form a white compound ($4\,CaO, Fe_2O_3$) which is readily decomposed by the feeblest acids. Sesquioxide of iron occurs native combined with oxide of zinc in crystals, mixed with oxide of manganese, constituting *Franklinite*. With protoxide of iron it forms the black or magnetic oxide of iron.

(637) *Black* or *Magnetic Oxide of Iron* (FeO, Fe_2O_3); *Sp. Gr.* 5·09.—This oxide occurs as a well-known mineral, the *loadstone*, which acquires its magnetism from the inductive influence of the earth. It is found in primitive rocks, forming beds, or sometimes as in Sweden, entire mountains. It furnishes a very pure and excellent iron, of which a large quantity is annually supplied from the Swedish and American mines: 100 parts of this oxide contain 72·41 of metal and 27·59 of oxygen. It has a black colour and metallic lustre; it crystallizes in cubes, octohedra, or rhombic

dodecahedra. Magnetic oxide of iron is the principal constituent of the scales of oxide which are detached during the forging of wrought iron. It fuses at a high temperature, and is formed when iron is burned in oxygen,—the sesquioxide which is the result of the action losing part of its oxygen, owing to the intensity of the heat developed during the combustion. The magnetic oxide is also formed by passing steam over heated iron turnings. A hydrate of this oxide (HO, FeO, Fe_2O_3) may be procured by dividing a freshly prepared solution of the sulphate of the protoxide of iron into three equal portions: two of these are heated to the boiling point, and to the boiling liquid nitric acid is gradually added so long as its addition causes the evolution of binoxide of nitrogen: when this point is reached, the whole of the protoxide of iron will have been converted into peroxide; $6\,(FeO,SO_3)+3\,(HO,SO_3)+HO,NO_5=3\,(Fe_2O_3,3\,SO_3)+NO_2+4\,HO$: the remaining portion of the solution of the protosulphate is then poured into the hot liquid, and carbonate of soda or caustic ammonia is added in slight excess: the solution and precipitate are boiled together, and the black oxide falls as a heavy crystalline powder. The magnetic oxide is soluble without difficulty in hydrochloric acid, as well as in nitric acid and in aqua regia; this oxide, however, does not form specific salts, but mixtures of salts of the protoxide and peroxide; $Fe_3O_4+4\,(HO,SO_3)$ becoming $FeO,SO_3+Fe_2O_3,3\,SO_3+4\,HO$.

If recently precipitated hydrated sesquioxide of iron, obtained from the sesquichloride by ammonia, be well washed, and without being dried be boiled with water and iron turnings in large excess, hydrogen is evolved, and magnetic oxide of iron formed.

(638) *Ferric Acid* ($HO,FeO_3=9+52$).—If a mixture of 1 part of sesquioxide of iron and 4 parts of nitre be heated to full redness for some time, a brown mass is obtained, which with water gives a beautiful violet-coloured solution, due to the presence of ferrate of potash. In this compound the iron is combined with a larger quantity of oxygen than in the sesquioxide, but the ferric acid has not been obtained in an insulated form. Ferrate of potash may be more easily procured by suspending 1 part of recently precipitated hydrated sesquioxide of iron in a concentrated solution of potash, consisting of 30 parts of hydrate of potash and 50 of water, and then transmitting a current of chlorine gas: the ferrate of potash is insoluble in a concentrated solution of potash, and is deposited as a black powder, which may be drained upon a tile (Fremy). This compound is very soluble in water, but is precipitated in black flocculi by a large excess of alkali. It is a very unstable salt: in dilute solutions the alkali becomes free, hydrated

sesquioxide of iron subsides, and oxygen escapes. Organic matter decomposes it speedily, just as it does the permanganate of potash: a temperature of 212° destroys it instantly if in solution, and the addition of an acid, even in quantity insufficient to neutralize the whole of the alkali, causes the immediate separation of oxygen, and precipitation of the sesquioxide of iron.

Ferrates of baryta, strontia, and lime may be obtained in the form of red insoluble precipitates, by admixture of solutions of the salts of the earths with a solution of the ferrate of potash.

(639) SULPHIDES OF IRON.—Sulphur combines with iron in several proportions: the protosulphide FeS, and the bisulphide FeS_2, are the most important; but besides these a disulphide (Fe_2S) has been obtained by heating sulphate of iron to redness in a current of hydrogen gas: a sesquisulphide, Fe_2S_3, may also be formed by precipitating the persalts of iron by the protosulphides of the alkaline metals; and two magnetic sulphides of iron (6 FeS, FeS_2) and (2 FeS, FeS_2) are found native.

Protosulphide, or *Sulphuret of Iron* (FeS=44), may be prepared by heating a bar of iron to whiteness and bringing it into contact with a roll of sulphur: immediate union takes place, and the resulting sulphide melts and runs down in drops of a reddish-brown colour: when formed in this manner it usually contains an excess of sulphur. It may also be prepared by projecting in successive portions, into a red-hot earthen crucible, a mixture of 7 parts of iron filings, with 4 parts of sulphur in fine powder; vivid deflagration occurs at the moment of combination. Protosulphide of iron dissolves both iron and sulphur if either be present in excess; its composition, therefore, is variable. Like carbon, the presence even of a minute portion of sulphur alters the quality of wrought iron, which if it contain even $\frac{1}{10,000}$ of sulphur is rendered 'red short.' Anhydrous protosulphide of iron is dissolved by diluted sulphuric or hydrochloric acid with evolution of sulphuretted hydrogen: this decomposition is frequently employed in the laboratory as a convenient source of sulphuretted hydrogen. Nitric acid and aqua regia decompose it and form pernitrate or perchloride of iron, setting part of the sulphur free, and converting the residue into sulphuric acid. When heated in the open air, this sulphide absorbs oxygen and becomes converted into sulphate of iron; at a still higher temperature it is decomposed, sulphurous and sulphuric acids escape, and sesquioxide of iron remains.

Protosulphide of iron may be obtained as a black hydrate, by precipitating a solution of a protosalt of iron with one of a protosulphide of one of the alkaline metals; thus $HO,KS + FeO,SO_3 = HO,$

$FeS+KO,SO_3$; in this condition it rapidly attracts oxygen from the air, and assumes a brownish-red colour, sesquioxide of iron being formed and sulphur liberated. When iron is present in very minute quantities in a solution, and is precipitated by a solution of hydrosulphate of ammonia, the very finely divided particles of sulphide of iron are apt to pass through the filter; the liquid then has a peculiar green tint.

If iron filings be mixed with two thirds of their weight of sulphur in powder, and moistened, the mixture becomes hot when exposed to the air, and absorbs oxygen with sufficient rapidity to cause it in many cases to inflame; sulphide of iron is at first formed, which quickly becomes converted into sulphate. A valuable lute for the joints of iron vessels is composed of a mixture of 60 parts of iron filings sifted fine, and 2 of sal ammoniac in fine powder intimately blended with 1 part of flowers of sulphur. This powder is made into a paste with water, and applied immediately; in a few minutes it becomes hot, swells, disengages ammonia and sulphuretted hydrogen, and soon sets as hard as iron itself.

(640) *Bisulphide of Iron* ($FeS_2=60$); *Sp. Gr.* 4·98.—This compound is found abundantly in the native state, constituting the *iron pyrites* of mineralogists. It occurs in the strata of every period: when found in the older formations it is crystallized in cubes, and sometimes in dodecahedra, of a brassy lustre, and is hard enough to strike fire with steel; but in the tertiary strata it more frequently occurs in fibrous radiated nodules. The formation of iron pyrites may occasionally be traced to the slow deoxidation of sulphates by organic matter in waters containing carbonate or other salts of iron in solution; it is then frequently deposited in cubes or octohedra. This appears to be the usual mode of its formation in alluvial soils. Some varieties of iron pyrites, especially those found in the tertiary strata, are speedily decomposed by exposure to air; oxygen is absorbed, and sulphate of protoxide of iron formed. This decomposition occurs with greater facility if the bisulphide be mixed with other substances, as is the case in the aluminous schists; in which by the further action of air, a subsulphate of the sesquioxide of iron is formed, whilst the liberated sulphuric acid reacts upon the alumina, magnesia, or lime of the soil, and forms sulphates; those of alumina and magnesia may be extracted by lixiviation. The ordinary crystallized pyrites from the older strata is not thus decomposed, but a variety of a whiter colour is rapidly disintegrated by exposure to the weather; this form of pyrites is known as *white iron pyrites*; it crystallizes in right rhomboidal prisms, but it possesses the same

chemical composition as the yellow cubes. Pure bisulphide of iron contains 53·33 per cent. of sulphur, and 46·67 of metallic iron.

Iron pyrites is not acted upon by cold sulphuric or by hydrochloric acid, but it is rapidly oxidized and dissolved by nitric acid and by aqua regia: boiling oil of vitriol dissolves it gradually with evolution of sulphurous acid. When heated in closed vessels it fuses, and sulphur is expelled. If heated in the air it burns with flame, peroxide of iron is formed, whilst sulphurous acid escapes in large quantity. This circumstance has been turned to account in the manufacture of oil of vitriol, for which purpose enormous quantities of *mundic*, as the bisulphide is termed by the workmen, are annually consumed. Iron pyrites may be prepared artificially by exposing a mixture of powdered protosulphide of iron with half its weight of flowers of sulphur, in a covered crucible to a heat below redness, as long as sulphurous fumes escape.

(641) *Magnetic Sulphide of Iron* ($6\,FeS,FeS_2$); *Sp. Gr.* 4·65. —This compound exhibits a brassy lustre, but is distinguished from ordinary pyrites by its solubility in hydrochloric acid. It is often formed when sulphur and iron are heated together in preparing the protosulphide for use in the laboratory. Another variety of magnetic pyrites consists of, $2\,FeS,FeS_2$.

Mispickel, or arsenical pyrites, is an arsenio-sulphide of iron ($FeS_2,FeAs$) which, amongst other localities, occurs abundantly in the Hartz, in Saxony, and in some of the Cornish mines; it crystallizes in right rhombic prisms, of a steel-grey colour and metallic lustre. When heated in closed vessels it is partially decomposed, and sulphide of arsenic sublimes. If exposed to a high temperature in the open air, it produces sesquioxide of iron, whilst arsenious and sulphurous acids escape. Analogous compounds of cobalt and nickel occur amongst the ores of these metals.

A remarkable class of compounds, termed by Roussin, who discovered them, *nitrosulphides of iron*, may be obtained by the reaction of nitrite of potash and hydrosulphate of ammonia upon the salts of iron. The reaction is complicated, and their properties will be better examined hereafter (1353 *a*).

Subphosphide of Iron (Fe_4P) may be obtained by reducing the phosphate of the metal with charcoal: it fuses at a red heat, and forms an extremely hard, brittle mass, which dissolves both phosphorus and iron in all proportions.

(642) CHLORIDES OF IRON.—Iron forms with chlorine two compounds, a protochloride, $FeCl$, and a sesquichloride, Fe_2Cl_3, which correspond in composition to the salifiable oxides of the metal.

Protochloride of Iron ($FeCl=63{\cdot}5$) *Sp. Gr. anhydrous,* 2·528; *cryst.* 1·926.—By passing dry hydrochloric acid gas over ignited metallic iron, the acid is decomposed, hydrogen gas escapes, chlorine combines with the iron, and a white anhydrous protochloride of the metal sublimes at a temperature at which glass begins to soften. Its solution may be formed by dissolving iron in hydrochloric acid; the hot, saturated liquid deposits the salt, on cooling, in green crystals, which contain 4 Aq. It is very soluble in water, and is taken up in considerable quantity by alcohol. If heated in the open air, chlorine escapes and peroxide of iron remains.

Protochloride of iron unites with chloride of ammonium and forms a double salt, from which the iron may be deposited upon various metallic articles, by boiling them in this solution with scraps of zinc; the zinc displaces the iron, which is deposited in a coherent lamina upon the other metals in consequence of a voltaic action.

Sesquichloride or *Perchloride of Iron* ($Fe_2Cl_3=162{\cdot}5$); *Sp. Gr. of Vapour,* 11·39.—This compound sublimes in anhydrous brown scales when dry chlorine gas is transmitted over iron heated to redness. The anhydrous chloride is very deliquescent, and hisses when thrown into water, forming a red solution. It is also soluble both in alcohol and ether. In a hydrated condition it may be procured by evaporating a solution of the protochloride through which chlorine has been passed to saturation, or by dissolving hydrated peroxide of iron in hydrochloric acid: the solution, by concentration, yields large, red, deliquescent crystals ($Fe_2Cl_3+6\,Aq$), but the salt cannot be rendered anhydrous by evaporation, as it is decomposed into hydrochloric acid and peroxide of iron. It also crystallizes in stellate, orange-coloured groups, with 12 Aq, which are less deliquescent than the other hydrate. Perchloride of iron forms a double salt with chloride of ammonium, which crystallizes readily in cubes, and is known in pharmacy as the *ammonio-chloride of iron.* The composition of this salt varies considerably: it is of a ruby-red colour, and seldom contains more than 2 per cent. of iron. Double salts of perchloride of iron with chloride of sodium and chloride of potassium may also be formed.

A hydrated *oxychloride of iron* is formed when a solution of the protochloride of the metal is exposed to the air, or when the perchloride is precipitated by a small quantity of caustic alkali. It is insoluble in water containing salts, but is partially soluble in pure water.

(642 *a*) The BROMIDES of iron correspond in composition to the chlorides.

Protiodide of Iron ($FeI=155$) is formed by digesting iron wire or filings, in a closed vessel, with four times their weight of iodine suspended in water; direct combination between the elements takes place, the iodide is dissolved and forms a pale green solution, which, by evaporation *in vacuo*, yields crystals containing 4 Aq. By a continued heat they may be rendered anhydrous, and in that state are fusible. By exposure to air, the solution absorbs oxygen and is decomposed; iodine is set free, and a hydrated oxyiodide of iron falls. This change is retarded by mixing the solution with strong syrup; and as the compound is employed in medicine, this method is frequently adopted to preserve uniformity in its composition. No definite *sesqui-iodide* of iron is crystallizable.

(643) PROTOSULPHATE OF IRON, *Copperas*, or *Green Vitriol*, (FeO,SO_3+7 Aq$=76+63$: *Sp. Gr. anhydrous*, 3·138, *cryst.* 1·857. —This salt is prepared in a state of purity by dissolving 1 part of pure iron, or $1\frac{1}{4}$ of its protosulphide, by the aid of heat, in $1\frac{1}{2}$ parts of oil of vitriol diluted with 4 of water. On filtering the solution quickly, it deposits beautiful, transparent, bluish-green, rhomboidal crystals on cooling, with 7 Aq. They effloresce in a dry air, and form a white crust, which soon becomes of a rusty-brown colour, owing to the absorption of oxygen and formation of a subsulphate of the sesquioxide. If crystallized at a temperature of 176° the protosulphate forms right rhombic prisms, which contain only 4 Aq. It may also be obtained crystallized with 3 and with 2 equivalents of water. For commercial purposes sulphate of iron is formed by the decomposition of iron pyrites, or of aluminous schists containing pyrites, as already described when speaking of the manufacture of alum. The sulphate of iron thus obtained has a grass-green colour, owing to the presence of persulphate of iron. Sulphate of iron is largely used in combination with astringent vegetable matters as a black dye; ordinary writing-ink is a compound of this kind.

This salt is insoluble in alcohol, and requires twice its weight of cold water for its solution. Its solubility is greater at 194° than at 212°, 100 parts of water dissolving 370 parts of the crystals at 194° and only 333 at the boiling point. This anomaly is probably dependent upon causes similar to those observed in the case of the sulphate and the carbonate of soda. If exposed to the air, the solution absorbs oxygen, and a rusty precipitate occurs, which is a basic persulphate composed of $2\ Fe_2O_3,SO_3+3$ Aq, while persulphate of iron remains in solution. Owing to its strong affinity for oxygen, protosulphate of iron is occasionally used as a

reducing agent: it is thus employed to precipitate gold and palladium in the metallic form from their solutions, and indigo is by its means brought into the soluble condition. If heated gradually, each atom of the crystallized protosulphate loses 6 atoms of water and forms a white powder; 1 atom of water being retained at all temperatures below 500°. At a red heat the sulphate is decomposed; a portion of the acid yields one third of its oxygen to the protoxide of iron, which is converted into the sesquioxide, whilst sulphurous acid escapes; the remainder of acid distils in the anhydrous form, $2(FeO,SO_3) = Fe_2O_3 + SO_2 + SO_3$; but as in practice the salt cannot be rendered anhydrous in large quantities, a little water distils with the sulphuric acid, which is condensed as a brown fuming liquid, the 'Nordhausen Sulphuric Acid' (346). The residual sesquioxide of iron is sold under the name of colcothar (636).

The aqueous solution of protosulphate of iron, in common with that of all the protosalts of this metal, absorbs a large quantity of binoxide of nitrogen; forming a deep brown solution, which has a powerful affinity for oxygen: if this solution be heated in closed vessels, the gas is for the most part expelled unchanged; if heated in air, nitric acid is formed in the liquid, and this converts the iron into a salt of the peroxide.

With the sulphates of potash and ammonia, green vitriol yields double salts precisely analogous in form and composition to those which are formed by these sulphates with sulphate of copper. The formula of the potash salt is $FeO,SO_3 + KO,SO_3 + 6$ Aq.

Persulphate or *Sesquisulphate of Iron* (Fe_2O_3, $3\ SO_3 = 200$) is made either by treating brown hæmatite with an excess of strong sulphuric acid, allowing it to digest for some time and then expelling the excess of acid at a heat short of redness; or by adding to the solution of 1 equivalent of protosulphate of iron, $\frac{1}{2}$ an equivalent of oil of vitriol, boiling, and peroxidizing the iron by adding to the solution nitric acid in small quantities as long as any red fumes are given off. A yellowish-white deliquescent mass is obtained on evaporation, from which the acid is expelled by a red heat; at a more moderate heat the salt is rendered anhydrous: water dissolves it but slowly. It is found native in large quantities in Chili in the form of a white powder (Fe_2O_3, $3\ SO_3 + 9$ Aq). Several hydrated subsulphates of the peroxide of iron may be obtained.

With sulphate of potash and the sulphates of the other alkalies persulphate of iron forms double salts, resembling common alum, in form and composition as well as in taste. The potash salt (KO,

$SO_3 + Fe_2O_3\ 3\ SO_3 + 24\ Aq$; *sp. gr.* 1·718) is astringent, very soluble in water, but insoluble in alcohol: it is very prone to spontaneous decomposition, and becomes converted from a colourless into a brown, gummy, deliquescent mass: this change is also produced by heating the salt to a temperature below 212°. The solution of the two sulphates should therefore be allowed to evaporate spontaneously during its preparation. The double salt with ammonia is much more permanent, and crystallizes readily in beautiful octohedra.

(643 *a*) PROTONITRATE OF IRON ($FeO,NO_5 + 6\ Aq$* $= 90 + 54$).—This salt may be obtained by dissolving protosulphide of iron in cold nitric acid diluted with 4 or 5 times its bulk of water. Sulphuretted hydrogen is evolved in abundance, and on evaporating the solution *in vacuo* over oil of vitriol, it crystallizes in pale-green rhombs, which when heated evolve binoxide of nitrogen and yield a basic nitrate of the sesquioxide $6\ (FeO_2,NO_5) = NO_2 + 3\ Fe_2O_3, 5\ NO_5$. This change sometimes occurs in warm weather spontaneously. The basic salt is then freely soluble in water, and is not decomposed by ebullition. Protonitrate of iron may also be procured by decomposing a solution of the protosulphate of iron by an equivalent quantity of nitrate of baryta. It cannot be obtained in a pure form by dissolving iron in diluted nitric acid; since in that case the metal is dissolved without evolution of gas, and ammonia is formed in the liquid:—

$$10\ (HO,NO_5) + 8\ Fe = 8\ (FeO,NO_5) + H_4NO,NO_5 + 6\ HO.$$

Pernitrate of Iron ($Fe_2O_3, 3\ NO_5$).—When nitric acid of sp. gr. 1·2 or 1·3 is digested upon metallic iron, a violent action occurs attended with the extrication of nitrous acid and of deutoxide of nitrogen; the iron is at the same time converted into peroxide, which combines with the acid, and is obtained with difficulty on evaporation in prismatic hydrated crystals. An insoluble basic nitrate is commonly formed at the same time.

(644) PROTOCARBONATE OF IRON ($FeO,CO_2 = 58$) is found native in immense quantities, forming a valuable ore of iron. In its less usual condition, when crystallized, it constitutes spathic iron ore, and occurs in yellowish lenticular crystals, the primary form of which is a rhombohedron, isomorphous with calcareous spar. It contains, when pure, 48·27 per cent. of metallic iron, or 62·07 of oxide of iron and 37·93 of carbonic acid. The native carbonate very often contains carbonate of manganese. The clay-iron ore, from which the greater part of the English iron is obtained, is, as

* Not 7 Aq, as is sometimes stated.

already mentioned, an impure carbonate of iron. Clay iron-stone, besides the more usual form of bands or seams accompanying the coal strata, occurs also in detached nodules or lumps, sometimes of very large size, imbedded in the clay of the same formations. When carbonate of iron is heated strongly in vessels from which air is excluded, carbonic acid and carbonic oxide are expelled and magnetic oxide of iron is left, the decomposition being as follows: $3\,(FeO,CO_2) = Fe_3O_4 + 2\,CO_2 + CO$. Carbonate of iron is the salt contained in most ferruginous springs, in which it is held in solution by free carbonic acid: it is rarely present in a larger quantity than 1 grain per pint. Mere exposure to air causes its separation; the acid escapes, oxygen is absorbed, and hydrated peroxide of iron, mixed with a small quantity of organic matter, subsides, forming the ochry deposits so usual around chalybeate springs. The protocarbonate of iron may be produced artificially by mixing a protosalt of iron with a carbonate of one of the alkalies, when it falls as a pale green voluminous hydrate which is speedily altered by exposure to air; it absorbs oxygen, rapidly losing its carbonic acid, and is converted into the red hydrated sesquioxide; during the process of drying it is therefore almost completely decomposed. No carbonate of the sesquioxide of iron appears to exist, but the bicarbonate of potash as well as that of soda dissolves the hydrated peroxide of iron; the red solution thus formed is very slowly decomposed by prolonged ebullition.

(644 *a*) OXALATES OF IRON.—*Protoxalate of Iron* ($2\,FeO,C_4O_6 + 3\,Aq$) is occasionally formed in the brown-coal strata, in yellow fibrous or granular masses, known as *Humboldtite* or *iron-resin*. It may be prepared artificially by precipitating the solution of protosulphate of iron by oxalate of ammonia; or by exposing a solution of peroxalate of iron in oxalic acid to the sun. Carbonic acid is then evolved, and the yellow protoxalate of iron with 4 Aq is thrown down as a yellow crystalline and nearly insoluble powder.

The *Peroxalate of Iron* is also a lemon-yellow powder, nearly insoluble in water, but soluble in excess of oxalic acid. It may be obtained by mixing a slight excess of a persalt of iron with one of a soluble oxalate.

The peroxalate of iron forms several double salts of the formula ($3\,MO,Fe_2O_3\,3\,C_4O_6$), analogous to the blue double oxalates of chromium (659 *b*). Potash, soda, ammonia, baryta, strontia, and lime salts have been obtained by digesting the acid oxalates of these bases upon hydrated oxide of iron. These double oxalates are all freely soluble. It is owing to the formation of the soluble

potash salt, that binoxalate of potash (salt of sorrel), is useful for removing stains of ink and oxide of iron from linen.

(645) PHOSPHATES OF IRON.—*Triprotophosphate of Iron* ($HO, 2 FeO,PO_5$), falls as a white powder on adding triphosphate of soda to a protosalt of iron; by exposure to air it absorbs oxygen, and becomes blue. A hydrated blue phosphate of iron is found native; it is known as *vivianite*. It is probably a mixture of phosphates of the protoxide and peroxide of iron [$HO, 2 FeO,PO_5 + 2 (Fe_2O_3, PO_5)$], and contains in addition about 30 per cent. of water.

A *sesquiphosphate* ($Fe_2O_3,PO_5 + 4 Aq$), is obtained as a white powder by decomposing sesquichloride of iron by an alkaline triphosphate. Exposure of this salt to air produces no change. It is insoluble in acetic acid, but soluble in peracetate of iron: phosphoric acid is sometimes precipitated in this form in the course of analysis. Its composition is said to vary according as the phosphate of soda or the salt of iron is in excess.

Several native *silicates of iron* are known, but they are not important. The 'finery slag' obtained in the conversion of cast into wrought iron consists chiefly of basic silicate of protoxide of iron ($2 FeO,SiO_2$). Oxide of iron rapidly attacks clay crucibles if fused in them.

(646) CHARACTERS OF THE SALTS OF IRON.—Iron forms two classes of salts, both of which are readily distinguished from each other and from those of other metals. The salts of iron are not poisonous, unless administered in excessive quantities; they form valuable tonics and astringents when taken internally. The solutions both of the protosalts and of the persalts have an inky, astringent taste.

1. *Salts of the Protoxide.*—These salts, when in solution, or when crystallized, have a pale-green colour; they redden litmus, but very feebly. With the *alkalies* a grey or green precipitate of hydrated protoxide is formed in their solutions; it passes quickly through various shades of green into brown by exposure to the air; this change of colour is due to the absorption of oxygen, in consequence of which the sesquioxide is eventually produced. If the precipitate be produced by *ammonia*, an excess of this reagent redissolves a part of the precipitate; and if the solution contains chloride of ammonium, the whole of the oxide will be redissolved: this solution absorbs oxygen rapidly from the air, and a film of sesquioxide of the metal is formed upon the surface. The protosalts of iron are not precipitated in slightly acid solutions by *sulphuretted hydrogen*; but they give a black precipitate of hydrated sulphide

on adding a solution of *hydrosulphate of ammonia*. *Ferrocyanide of potassium* gives a pale blue precipitate, which, on exposure to the air, deepens in tint, owing to the absorption of oxygen. *Red prussiate of potash,* when added to a neutral or acid solution gives a bright-blue precipitate, which is one of the varieties of Prussian blue. If a solution of a protosalt of iron be boiled with *nitric acid,* the metal is completely converted into a salt of the peroxide: the same thing is effected by the action of chlorine or of bromine, or by boiling an acidulated solution of the salt with a small quantity of chlorate of potash.

2. *Salts of the Peroxide.*—In solution they have a yellow or reddish-brown colour. *Hydrosulphuric acid* reduces them to the state of protosalts, whilst a white deposit of sulphur occurs: for example, with the persulphate the following reaction takes place:— $Fe_2O_3, 3\ SO_3 + HS = 2\ (FeO,SO_3) + HO,SO_3 + S$. With *hydrosulphate of ammonia* a black hydrated sesquisulphide of iron is precipitated. The *alkalies* give a reddish-brown voluminous precipitate of hydrated peroxide, insoluble in excess of alkali. *Sulphocyanide of potassium* in neutral or acid solutions gives an intense blood-red solution; *yellow prussiate of potash,* a bright blue precipitate of ordinary Prussian blue. *Red prussiate of potash* occasions no precipitate in solutions of the persalts of iron, but the liquid acquires a greenish hue; the persalts may thus be distinguished from the protosalts of the metal. *Tincture of galls,* in neutral solutions, yields a bluish-black inky precipitate; this test is rendered much more delicate in its indications by the addition of water holding a little bicarbonate of lime in solution: it is the colouring matter of ordinary writing ink. In neutral solutions the *benzoates* and the *succinates* of the alkalies give voluminous insoluble precipitates: benzoate or succinate of ammonia or potash is sometimes employed to separate iron from nickel and cobalt, as the benzoates and the succinates of these metals are soluble. If a solution of a persalt of iron to which an alkali has been added till it begins to occasion a permanent precipitate be raised to the boiling point, it is completely decomposed, and an insoluble subsalt of iron is precipitated: this property is often turned to account in the separation of iron from cobalt, nickel, and manganese, which are not precipitated under similar circumstances. When a persalt of iron in solution is digested with a bar of zinc in a flask provided with a tube for the escape of the gas, the zinc becomes oxidized, hydrogen is evolved, and the whole of the iron is precipitated as peroxide, whilst a salt of zinc is formed in the liquid.

Before the blowpipe both classes of the salts of iron act alike:

with borax in the reducing flame they give a green glass, which becomes colourless, or yellowish (if the iron be in large quantity) when held in the oxidating flame.

(647) *Estimation of Iron.*—In estimating the quantity of iron for the purposes of analysis, it should always be first converted into a persalt, by boiling with nitric acid or otherwise, after which it may be precipitated by excess of ammonia, and then well washed and ignited: pure sesquioxide of iron remains, consisting in 100 parts of 70 of iron and 30 of oxygen. Iron is thus readily separated from the alkalies and alkaline earths. If magnesia be present, it is apt to be partially precipitated with the oxide of iron, unless the solution contain a considerable quantity of chloride of ammonium. In the presence of tartaric acid, of sugar, and of various other forms of organic matter, ammonia precipitates the peroxide of iron very imperfectly from its solutions: in such a case hydrosulphate of ammonia must be employed. The iron is thus thrown down completely as sulphide; this precipitate must be redissolved in nitric acid, and then the iron may be obtained as peroxide by adding an excess of ammonia to the solution.

(648) *Separation of Iron from Alumina and Glucina.*—If alumina and glucina are contained in the liquid, they accompany the peroxide of iron when precipitated by ammonia. When these earths are present, the precipitation should be effected by an excess of caustic potash instead of by ammonia; the precipitate should be gently warmed with the liquid for the purpose of dissolving out the earths. The solution is filtered from the peroxide of iron, which requires long washing with boiling water to remove the last traces of potash. The alumina and glucina are obtained from the alkaline filtrate by neutralizing it with hydrochloric acid, and then adding a slight excess of ammonia; the alumina and glucina are precipitated together, and must be separated in the manner described in (578).

(649) *Separation of Iron from Zinc, Cadmium, Cobalt, Nickel, and Manganese.*—Having precipitated the cadmium by sulphuretted hydrogen, and reconverted the iron into peroxide by boiling the liquid with a small quantity of nitric acid, the solution is to be largely diluted with water, and carbonate of soda added gradually to the acid liquid until a permanent precipitate is formed, though the liquid remains acid. The solution must be boiled, and the liquid filtered from the bulky precipitate of the subsalt of iron: the clear solution must then be slightly supersaturated with carbonate of soda, and afterwards feebly acidulated with acetic acid: on again boiling the liquid, the last trace of iron is thrown down

in the form of basic acetate, whilst the other metals are retained in the solution: the precipitated salt of iron must be redissolved in hydrochloric acid, and the iron thrown down as peroxide by the addition of ammonia.

Sometimes ammonia in excess is made use of to separate iron from these metals, which all form soluble compounds with ammonia, and which, it is supposed, will retain them in solution; but this method should never be resorted to in analysis, because the oxide of iron always retains a large quantity of the other oxides.

(650) *Separation of Iron from Uranium.*—The iron having been converted into peroxide is precipitated by a large excess of carbonate of ammonia, which retains most of the uranium. This process, however, although usually adopted, is imperfect: for, if the quantity of iron be at all large, a considerable proportion of uranium is precipitated along with it.

(651) *Estimation of a Mixture of Protoxide and Peroxide of Iron.*—It often happens that the chemist has to ascertain the relative proportions of protoxide and sesquioxide of iron which a compound contains. If the compound of iron for examination be soluble in hydrochloric acid, the following process by Penny will be found both easy in execution and accurate in its results. It is based upon the power which a solution of bichromate of potash in excess of hydrochloric acid possesses of converting protochloride of iron into sesquichloride, while the chromic acid is reduced to the state of sesquichloride of chromium, in the manner shown by the following equation:—

$$KO, 2CrO_3 + 6\,FeCl + 7\,HCl = 3\,(Fe_2Cl_3) + Cr_2Cl_3 + KCl + 7\,HO.$$

In order to carry this process into effect, 44·4 grains of pure bichromate of potash are introduced into an alkalimeter burette (480), which is to be filled up to 0° with tepid water; the mixture is to be agitated until the salt is dissolved. Each division of the instrument contains sufficient of the bichromate to convert half a grain of metallic iron, present in the form of protochloride of iron, into sesquichloride. The ore for experiment having been reduced to an extremely fine powder, 100 grains of it are boiled in a flask for ten or fifteen minutes with about 2 ounces of hydrochloric acid of sp. gr. 1·100: about 6 ounces of boiling distilled water are added, and the mixture immediately transferred to an evaporating basin, taking care to rinse out the flask thoroughly. A white plate is then spotted over with a few drops of a weak solution of red prussiate of potash, and the bichromate is cautiously added from the alkalimeter to the solution of iron (which is kept in con-

tinual agitation), until it assumes a dark greenish shade; as soon as this begins to appear, it must be tested after each addition of the bichromate, by taking out a drop of the solution on a glass rod, and adding it to one of the drops of the red prussiate. When the last drop no longer occasions a blue precipitate, the operation is ended, and the number of divisions of the liquid which has been added, when divided by two, indicates the amount of metallic iron which exists in the form of protoxide in 100 parts of the ore. The total quantity of iron present in the solution may be ascertained by making a second experiment on a fresh portion of the ore, and reducing the metal whilst still in the flask with the hydrochloric acid, to the state of protoxide: this is readily effected, either by transmitting a current of sulphuretted hydrogen and then expelling the excess of that gas by ebullition, or by boiling the concentrated solution with metallic zinc, or by nearly neutralizing the liquid with potash, and adding a solution of sulphite of soda until a drop of the liquid ceases to give a red colour when mixed with a drop of a solution of sulphocyanide of potassium,* placed upon a white plate: the liquid is then boiled, to expel the excess of sulphurous acid. When the iron has thus been reduced to the state of protoxide, the whole quantity of the metal present may be ascertained by means of the solution of bichromate of potash, as before; the difference between the two results will give the percentage of metallic iron present in the form of peroxide.

Another excellent process for determining the amount of a protosalt of iron present was contrived by Margueritte (*Ann. de Chimie*, III. xviii. 244). It consists in ascertaining the quantity of a measured solution of permanganate of potash of known strength, which the cold acidulated and largely diluted solution of iron in hydrochloric acid, can deoxidize and deprive of colour, owing to the reaction expressed in the following equation:—

$$KO,Mn_2O_7 + 10\,FeCl + 8\,HCl = 2\,MnCl + KCl + 5\,Fe_2Cl_3 + 8\,HO.$$

The strength of the solution of permanganate is ascertained by dissolving 5 grains of clean iron wire in boiling hydrochloric acid, diluting the solution largely, and ascertaining the number of divisions of permanganate measured from a burette, which it is capable of decolorizing.

The total quantity of iron present in an ore or other compound may be ascertained by a second experiment upon a fresh portion

* The reducing effect of sulphite of soda on the perchloride of iron may be explained by the following equation, from which it will be seen that the sulphite is converted into sulphate of soda during the operation:—

$$Fe_2Cl_3 + HO + NaO,SO_2 = 2\,(FeCl) + HCl + NaO,SO_3$$

of the ore, reducing the iron to the state of a salt of the protoxide by means of zinc, or otherwise, as described when treating of Penny's process.

(652) *Analysis of Cast Iron, Steel, and Bar Iron.*—For this purpose the metal must be reduced to a fine state of subdivision by means of a new file, previously freed from oil by the action of a solution of potash; the fine particles detached are to be sifted through a lawn sieve. Some kinds of cast iron are too hard to admit of being filed; they must be crushed in a small mortar made of hard steel.

1.—The proportion of *carbon* is ascertained by mixing from 50 to 100 grains of finely-divided iron with about 10 times its weight of chromate of lead or of oxide of copper; then placing it in an apparatus similar to that shown in fig. 265, and burning the iron in a very gentle current of oxygen; the carbonic acid which is formed is collected in a solution of potash placed in Liebig's bulbs. The tube which contains the iron is gradually heated with charcoal, commencing at the extremity nearest the potash bulbs, and the fire is slowly advanced towards the other end, until, when the operation is completed, the whole length of the tube is red hot. From the quantity of carbonic acid thus obtained, the proportion of carbon in the iron may be calculated.* But it has been already explained that cast iron contains carbon partly in chemical combination, partly in a state of mechanical mixture, and it is important to determine the relative proportions of the carbon which exist in these different conditions. This may be effected by dissolving the iron in hydrochloric acid. In this operation all the carbon which was chemically combined with the iron is separated in the form either of a gaseous compound of carbon and hydrogen, or as a liquid hydrocarbon; whilst the scales of graphite mechanically diffused through the metal are not acted upon by the acid, and are left in a solid form mixed with silica. In order to ascertain the proportion of graphite in this residue, it is collected on a small weighed filter, and washed with ether, to remove any adhering liquid hydrocarbon; the filter and its contents are dried at 212°, and weighed in a covered crucible. The residue is then burned, and the silica which remains is deducted from the weight of the precipitate collected on the filter.

* A less rapid but accurate plan consists in digesting the iron in filings or in fragments with an excess of neutral chloride of copper dissolved in water; the iron is slowly dissolved, and copper precipitated in its place, whilst the carbon is left in a finely divided condition. The precipitate must be collected on a filter, dried, and transferred to a tube in which it is burned, as above directed.

2.—The quantity of *silicon* contained in the iron is ascertained by dissolving the metal in hydrochloric acid and evaporating the solution to dryness, moistening with concentrated hydrochloric acid, then dissolving all the soluble matter in water, and collecting the silica on a filter: from this residue, after the graphite is burned off, the quantity of silicon can be estimated, 100 parts of silicic acid representing 48 of silicon.

3.—*Sulphur, Phosphorus,* and *Arsenic.*—The most accurate mode of estimating these substances consists in deflagrating about 50 grains of the finely-divided iron with about six times its weight of a mixture of 5 parts of pure nitre, and 1 part of carbonate of potash, in a crucible of silver, or, still better, of gold.* The phosphorus, sulphur, and arsenic are thus converted into phosphoric, sulphuric, and arsenic acids, which combine with the potash; when the fused mass is digested in water they are dissolved, whilst the peroxide of iron remains undissolved. The filtered solution is supersaturated with hydrochloric acid, and the sulphuric acid is thrown down by means of chloride of barium; the excess of baryta is removed by adding sulphuric acid, and the arsenic is thrown down by a current of sulphuretted hydrogen. The liquid, filtered from sulphide of arsenic, is now neutralized by ammonia, and on the addition of a few drops of solution of sulphate of magnesia, the phosphoric acid is gradually separated, on standing, as the crystalline double phosphate of magnesia and ammonia.

The sesquioxide of iron is dissolved in hydrochloric acid, and a current of sulphuretted hydrogen is transmitted, by which copper would be separated as sulphide; the filtrate is boiled with nitric acid, and the iron separated from manganese, cobalt, or nickel, by means of carbonate of soda in the manner already described (649).

§ VII. Chromium ($Cr=26 \cdot 27$). *Sp. Gr.* 6·81.

(653) Chromium is a metal which is but sparingly distributed over the earth. Its most important ore is the chrome ironstone, a compound of protoxide of iron with sesquioxide of chromium (FeO, Cr_2O_3), which has now and then been met with crystallized in regular octohedra like the magnetic oxide of iron, to which it corresponds in composition, but is more generally found massive: it is principally supplied from the United States and from Sweden. Occasionally the metal occurs in a higher state of oxidation, in

* Any traces of vanadium or of chromium would also be oxidised, and on digesting the mass in water would be dissolved out in the alkaline liquid.

combination with oxide of lead, as chromate of lead (PbO,CrO_3). Indeed it was in this beautiful mineral that Vauquelin, in the year 1797, first discovered the existence of chromium.

To obtain the metal, oxide of chromium is intimately mixed, in fine powder, with charcoal, and made up into a paste with oil; it is then placed in a crucible lined with charcoal, and the cover of the crucible is luted on, after which it is exposed for two hours to the heat of a good wind furnace; an agglomerated mass, of metallic appearance, is thus obtained. It is not pure chromium, but consists of a combination of carbon with the metal. Chromium obtained by this method is very difficult of fusion; it generally forms a porous mass composed of brilliant grains, which are hard enough to scratch glass. In this state it has a specific gravity of about 5·9, which is no doubt lower than it would be after complete fusion. Deville found on reducing chromium from pure sesquioxide by means of charcoal from sugar, in quantity insufficient for complete reduction, that the mass underwent partial fusion, but could not be melted into a compact button even at a temperature sufficient to fuse and volatilize platinum. If ignited with the alkalies, alkaline carbonates, or nitrates, chromium is rapidly converted into chromic acid, which combines with the alkaline base. It may, however, be heated to redness in the open air without becoming oxidized, and is not acted on by any acid except hydrochloric acid.

Fremy transmits the vapour of sodium over the sesquichloride, which is placed in a porcelain tray, and heated to redness in a porcelain tube: the chromium is obtained in brilliant crystals, which belong to the regular system; they are insoluble in aqua regia. Wöhler reduces chromium from the violet chloride by fusing it with twice its weight of zinc under a flux of the mixed chlorides of potassium and sodium: nitric acid is employed to dissolve the zinc, and the chromium is left as a grey brilliant crystalline powder of sp. gr. 6·81. If the sesquichloride be mixed with potassium, and heated in a covered crucible, another modification of chromium may be procured; after washing the residue with water, the metal remains in the form of a dark-grey powder, which assumes a metallic lustre under the burnisher. This pulverulent chromium, if heated in the air, takes fire below redness, and burns brilliantly: it is oxidized with great violence by nitric acid, sometimes becoming incandescent during the action; and it is dissolved by hydrochloric acid and diluted sulphuric acid, with evolution of hydrogen.

Metallic chromium has not been applied in the arts, but its

oxide and many of the chromates are highly valued as colouring materials, both in painting on porcelain and in calico printing.

(654) COMPOUNDS OF CHROMIUM WITH OXYGEN.—Chromium forms four well-marked oxides; a protoxide, CrO, and a sesquioxide, Cr_2O_3, both capable of forming salts with acids: an intermediate oxide (CrO,Cr_2O_3), corresponding to the magnetic oxide of iron, and a powerful metallic acid (CrO_3), chromic acid, corresponding to manganic and ferric acids. It also appears to be probable that a perchromic acid (Cr_2O_7) exists; at least, a blue liquid, which is soluble in ether, is obtained on pouring binoxide of hydrogen into a solution of chromic acid; but none of its compounds are known.

Protoxide of Chromium ($CrO=34{\cdot}3$).—This oxide is known only in the hydrated condition. It is obtained as a dark-brown precipitate on adding caustic potash to a solution of the protochloride of chromium; it absorbs oxygen with great avidity, and even decomposes water with extrication of hydrogen, and then becomes converted into the intermediate hydrated oxide (CrO, Cr_2O_3,HO), which is of the colour of Spanish snuff.

The protoxide of chromium forms a double sulphate with sulphate of potash ($CrO,SO_3+KO,SO_3+6\,Aq$), corresponding to the double sulphate of iron and potash both in form and composition. The crystals are of a fine blue colour.

(655) *Sesquioxide of Chromium* ($Cr_2O_3=76{\cdot}5$); *Sp. Gr. cryst.* $5{\cdot}21$.—This oxide is obtained as a greyish-green hydrate, by boiling with alcohol a solution of bichromate of potash acidulated with sulphuric acid. The alcohol deprives the chromic acid of half its oxygen, and the liquid becomes green from the formation of a sulphate of the sesquioxide. A current of sulphurous acid may be employed instead of alcohol in the reduction of chromic acid. On the addition of ammonia, a bulky, gelatinous, green precipitate of the hydrated oxide is produced, which, when dried in the air, has the formula (Cr_2O_3, 10 HO). In this form it is freely soluble in acids, and forms salts the solutions of which are of a green colour; but they do not crystallize.

Sesquioxide of chromium, though comparatively a feeble base, forms also another metameric set of soluble salts, which are of a violet colour and crystallize readily. If these violet-coloured salts be precipitated by an alkali, they give a bluish-green hydrated oxide, which if redissolved in an acid without the application of heat, reproduces the violet-coloured salts. This precipitated oxide easily passes into the green modification by the action of boiling water, or of concentrated saline solutions, upon it, or even by

strong friction. If a solution of one of the violet salts be heated to the boiling point, or a little short of it, the salt passes at once into the green modification. The oxide from the violet salts, the *metachromic* oxide of Fremy ($Cr_2O_3 + 9\,HO$, dried *in vacuo*), is soluble in excess of ammonia and in acetic acid; by long digestion with strong ammonia in the presence of an ammoniacal salt, the green modification of the oxide passes into the violet, and is dissolved by the alkali. Potash and soda precipitate the hydrated sesquioxide from both varieties, and redissolve it if added in excess, forming a green solution, from which, on boiling, the whole of the sesquioxide of chromium is separated as the hydrate of the green salts. When either of these hydrated oxides is heated, it parts with its water below redness, after which it is much less soluble in acids. If heated a little beyond this point, it suddenly becomes incandescent, shrinks considerably in bulk, and is no longer attacked by acids.

Besides the two soluble varieties of the salts of chromium before mentioned, a third, anhydrous, insoluble series is known, corresponding, it would seem, to the dense and comparatively inert modification of the metal itself.

The anhydrous green oxide of chromium is not decomposed by heat, and hence is used as a green colour in enamel painting. It is usually prepared for this purpose by decomposing subchromate of mercury by a red heat: half the oxygen of the acid is expelled along with the oxide of mercury. Chromate of ammonia may be employed instead of chromate of mercury with equally good results. Another method consists in strongly igniting, in a covered crucible, an intimate mixture of 4 parts of powdered bichromate of potash and 1 part of starch; the carbonate of potash resulting from the decomposition is washed out, and the sesquioxide of chromium which remains, after undergoing a second calcination, yields a beautiful clear green colour. There are also a variety of other modes of obtaining it. Sesquioxide of chromium is the colouring ingredient in greenstone, in the emerald, in pyrope, and in several other minerals. The *pink colour* used on earthenware is prepared by heating to redness a mixture of 30 parts of peroxide of tin, 10 of chalk, and 1 part of chromate of potash; the product is then finely powdered, and washed with weak hydrochloric acid; a beautiful rose-tint is thus obtained.

(655 *a*) *Chrome iron-stone* (FeO,Cr_2O_3; *Sp. Gr.* 4·5) is the principal ore of chromium: it corresponds in composition to the brown oxide of chromium and to the magnetic oxide of iron. Like the latter, it crystallizes in octohedra, which have about the same

hardness as felspar. Chrome iron-stone is scarcely attacked by any of the acids. It is infusible in the furnace, and when heated absorbs oxygen from the air; this oxidation takes place rapidly when it is powdered and mixed with a carbonate of one of the alkalies or alkaline earths, chromic acid being formed. 100 parts of this ore, if pure, contain 48·27 of chromium, and yield 89·6 of chromic acid.

(655 *b*) Fremy (*Comptes Rendus*, Dec. 6, 1858) has described a series of ammoniated compounds of chromium presenting some analogy with those of cobalt. If a solution of sal ammoniac containing free ammonia be digested on the hydrated oxide precipitated by ammonia from one of the violet salts of chromium, the oxide is dissolved and a fine violet-coloured solution is formed. If the compound thus formed by muriate of ammonia be evaporated to dryness it furnishes a fine violet compound, which is very soluble in water, has scarcely any alkaline reaction, and gives no precipitate with nitrate of silver; the ordinary tests of chromium do not show the presence of the metal. When the solution is boiled ammonia is expelled and hydrated oxide of chromium is precipitated. The decomposition indicates the existence of the elements ($3\,Cr_2O_3, 4\,H_3N, 2\,H_4NCl,HO$) in this compound.

When the aqueous solution of this body is exposed to the air, ammonia escapes and an insoluble violet-coloured substance is deposited in transparent rounded grains ($Cr_2O_3,H_3N\,12\,HO$); boiling water causes its decomposition: when this body is treated with acids a new class of ammoniated salts, termed from their colour *roseo-chromic*, is formed of the general formula ($Cr_2O_3, 4\,H_3N$) $3\,\bar{A}$, in which $\bar{A}$ represents any monobasic acid. The formation of the sulphate may be represented by the following equation:—

$$4(Cr_2O_3H_3,N) + 12SO_3 = 3\,\overbrace{(Cr_2O_3,3\,SO_3)}^{\text{Sulphate chromium.}} + \overbrace{(Cr_2O_3, 4\,H_3N) + 3\,SO_3}^{\text{Sulphate of roseo chromia.}}.$$

(656) Chromic Acid ($CrO_3 = 50·3$); *Sp. Gr.* 2·676.—There are several modes of obtaining this compound. 1.—The simplest consists in mixing 4 measures of a cold saturated solution of bichromate of potash with 5 of oil of vitriol: as the liquid cools, the chromic acid separates in beautiful crimson needles; for though very soluble in water, the acid has the peculiarity of being nearly insoluble in sulphuric acid of sp. gr. 1·55, but is freely dissolved by it either in a more concentrated or in a more dilute condition. The crystals are allowed to dry upon a porous tile, under a bell-glass. A good deal of sulphuric acid, however, still adheres to them; in order to remove it, the crystals should be dissolved in

water, and a solution of bichromate of baryta should be added in quantity just sufficient to throw down the whole of the sulphuric acid as sulphate of baryta: the solution may be recrystallized by evaporation *in vacuo*. 2.—Chromic acid may also be prepared from the terfluoride of chromium, by decomposing this compound with water (658).

Chromic acid when dried at a gentle heat is anhydrous. While hot it is black, but it becomes dark red on cooling: at about 400° it fuses, and if heated more strongly, becomes vividly incandescent, and is converted into the sesquioxide with disengagement of oxygen. Chromic acid deliquesces when exposed to the air. It has a sour, metallic taste, and possesses considerable oxidizing power, from the facility with which it is reduced to sesquioxide of chromium. When heated with hydrochloric acid, chlorine is evolved and chloride of chromium is formed; $2\,CrO_3 + 6\,HCl = Cr_2Cl_3 + 6\,HO + 3\,Cl$. Chromic acid forms more than one crystalline compound with sulphuric acid; these compounds are decomposed by water.

Chromates.—Chromic acid combines with bases, and forms three classes of salts—basic, normal, and acid.* The chromates of the alkalies are soluble in water; the normal salts have a yellow colour; the acid salts are of a bright orange: the most important of these salts are the chromate and bichromate of potash, from which the other chromates are generally obtained.

The *Bichromate of Potash* ($KO, 2\,CrO_3 = 147{\cdot}5$; *Sp. Gr.* 2·624) crystallizes in large red, transparent, anhydrous four-sided tables. It fuses below redness, and as it cools splits to pieces from the inequality of its contraction. It requires about 10 times its weight of water at 60° for its solution.

In order to procure the bichromate of potash, chrome ironstone is reduced to an extremely fine powder, and heated in a reverberatory furnace with carbonate of potash and a small proportion of nitre, the mixture being constantly stirred, to hasten the oxidation. When this is complete, the product is digested in water, and the yellow solution is drawn off from the insoluble matter; it is then supersaturated with nitric acid; a portion of silica is thus precipitated, and after this has been separated, the liquid, on evaporation, yields crystals of bichromate of potash, which are purified by recrystallization.

According to Schweitzer several double salts may be formed by digesting bichromate of potash with an equivalent of some other

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* If sulphuric acid be dibasic, the chromic, manganic, and ferric acids must be admitted to possess a similar composition, and the formulæ of their compounds must be doubled.

base, such as lime or magnesia. The chromate of magnesia and potash crystallizes in oblique rhombic prisms ($KO,MgO, 2\,CrO_3 + 2\,HO$) and a salt of similar composition may be obtained with lime; but there is no analogy between these double chromates and the magnesian double sulphates.

If a solution of carbonate of potash be added to the bichromate, until it becomes of a pale yellow colour, carbonic acid is expelled, and the *normal* or *neutral chromate* ($KO,CrO_3 = 97{\cdot}3$; *Sp. Gr.* 2·682) is formed. This salt is soluble in about twice its weight of cold water, and still more freely so in boiling water; it has a pure and intense yellow colour. A very small quantity of the salt suffices to impart a yellow tinge to a considerable volume of water. By evaporation of its solution chromate of potash may be obtained with some difficulty, in transparent, yellow, anhydrous prisms, which are isomorphous with those of sulphate of potash: at a red heat it fuses without undergoing decomposition. A *terchromate of potash* ($KO, 3\,CrO_3$), also anhydrous, was obtained by Mitscherlich in deep red crystals, by adding an excess of nitric acid to a solution of the bichromate, and allowing it to evaporate.

Chromate of Soda ($NaO,CrO_3 + 10\,Aq = 81{\cdot}3 + 90$) may be obtained by a process similar to that employed in preparing chromate of potash: it forms efflorescent crystals: a *bichromate* of soda may likewise be formed.

Chromate of Lime is soluble, as is also the *Bichromate*, which is formed in many chrome works as a preliminary stage in the manufacture of the chromates. Jacquelain decomposes chrome ore by roasting it in fine powder intimately mixed with chalk, grinds the roasted mass with water, and adds sulphuric acid till the liquid has an acid reaction, in which case bichromate of lime is formed, and remains in solution. *Chromate of baryta* (BaO,CrO_3) is a canary-yellow insoluble powder. *Chromate of strontia* is yellow and but slightly soluble.

Chromate of Lead ($PbO,CrO_3 = 162{\cdot}3$; *Sp. Gr.* 5·653) forms the pigment called 'chrome yellow.' It is obtained by precipitating a somewhat dilute solution of acetate of lead by one of chromate, or of bichromate of potash. Chromate of lead is insoluble in water and in acids, but, like all the insoluble salts of lead, it is dissolved by a large excess of potash or of soda. When heated to 400° or 500°, its colour becomes reddish brown; at a higher temperature it fuses, and when heated still more strongly it gives off oxygen, sesquioxide of chromium and subchromate of lead being formed, $4\,(PbO,CrO_3) = 2\,(2PbO,CrO_3) + Cr_2O_3 + O_3$. Fused

chromate of lead when reduced to powder is sometimes advantageously substituted for oxide of copper in the combustion and analysis of organic substances very rich in carbon. A *Dichromate of Lead* ($2\,PbO,CrO_3$; *Sp. Gr.* 6·266), of a splendid scarlet colour, may be obtained by boiling a solution of the yellow chromate of lead with half an equivalent of lime, or by adding to a solution of nitrate of lead a solution of chromate of potash, with which an additional equivalent or hydrate of potash has been previously mixed. It may be obtained of a still more brilliant colour by fusing 1 part of the neutral chromate of lead with 5 parts of nitre; chromate of potash and dichromate of lead are formed; the salt of potash may be removed by washing. This salt is used to impart a permanent orange to calico: it is easily fixed upon the fabric by dyeing it yellow with chromate of lead and then boiling it with lime-water, by which half the chromic acid is abstracted, and the dichromate is left attached to the fibre.

Subchromate of Mercury ($4\,Hg_2O, 3\,CrO_3$), falls as an orange-coloured insoluble precipitate on adding subnitrate of mercury to a soluble chromate. *Chromate of silver* (AgO,CrO_3; *Sp. Gr.* 5·770), is of a dark-red colour, the tint of which is deeper if the solutions be mixed whilst hot: it is crystalline, and sparingly soluble.

A bichromate of silver is obtained in beautiful crimson tables by heating metallic silver with bichromate of potash and sulphuric acid, chrome alum being formed during the process:—

$$3\,Ag + 4\,(KO, 2\,CrO_3) + 7\,(HO,SO_3) = 3\,(AgO, 2\,CrO_3) + (KO,SO_3 + Cr_2O_3, 3\,SO_3) + 3\,(KO,SO_3) + 7\,HO.$$

Chromic acid is the colouring matter of the ruby.

Bichromate of Chloride of Potassium ($KCl, 2\,CrO_3$).—This remarkable compound may be obtained crystallized in orange-coloured needles, by dissolving 3 parts of bichromate of potash and 4 of hydrochloric acid in a little water at a gentle heat, and allowing it to cool; a large quantity of water decomposes the salt.

(656 *a*) *Sesquisulphide of Chromium* ($Cr_2S_3 = 100{\cdot}5$).—This compound may be obtained in black shining scales, resembling plumbago in appearance, when the vapour of bisulphide of carbon is transmitted over sesquioxide of chromium strongly heated in a porcelain tube. The affinity of chromium for sulphur is but slight. If the hydrosulphate of ammonia be mixed with a salt of the sesquioxide of chromium, the hydrated sesquioxide of the metal is precipitated, whilst sulphuretted hydrogen is evolved.

(657) COMPOUNDS OF CHROMIUM WITH CHLORINE.—Chromium forms two chlorides, a protochloride and a sesquichloride:

the latter is the more important. It also forms an oxychloride $(CrClO_2)_2$, frequently termed chlorochromic acid.

The *Protochloride* ($CrCl=61 \cdot 7$) is obtained by heating the sesquichloride to redness in a current of dry hydrogen (carefully freed from every trace of oxygen); it is a white substance which is readily dissolved by water, forming a blue solution which rapidly absorbs oxygen, and becomes green: like the protochloride of iron, it absorbs binoxide of nitrogen quickly and becomes brown.

Sesquichloride of Chromium ($Cr_2Cl_3=159$).—When a current of dry chlorine is transmitted over an intimate mixture of finely divided sesquioxide of chromium and charcoal, heated to redness in a glass tube, beautiful pale violet-coloured scales of the anhydrous sesquichloride of the metal sublime. When rubbed upon the skin they have a soapy feel; they are quite insoluble in cold water, but by boiling them with water for some time a green solution is gradually formed. Sulphuric and hydrochloric acids, and even aqua regia, do not dissolve them. It is, however, very remarkable that the change from this insoluble to the soluble green variety is effected in a few moments with extrication of heat, by the addition of a minute quantity of the protochloride of chromium to the insoluble chloride when it is suspended in water. When the green hydrated sesquioxide of chromium is dissolved in hydrochloric acid a similar green solution is formed: the liquid furnishes, by spontaneous evaporation, green crystals, which may be represented, according to Péligot, as consisting of (Cr_2O_2Cl, 2 $HCl+10$ HO); for it is singular that only two thirds of the chlorine which this solution contains is precipitated when it is mixed with nitrate of silver (*Ann. de Chimie,* III. xii. 536; xiv. 239, and xvi. 294). A violet chloride of the metal which contains the same proportion of chlorine may be formed by precipitating the violet-coloured sulphate of chromium by an equivalent quantity of chloride of barium: nitrate of silver precipitates the whole of the chlorine from this solution.

Several oxychlorides of chromium may be formed.

(657 *a*) *Chlorochromic Acid* $(CrClO_2)_2$, or ($CrCl_3$, 2 CrO_3); *Sp. Gr. of vapour,* 5·52; *of liquid,* 1·71; *Comb. vol.* 4; *Boiling pt.* 250°. —This is a dense red liquid, which emits copious red fumes, of a suffocating odour; it is immediately decomposed by water into chromic and hydrochloric acids. When dropped into a strong solution of ammonia or into alcohol, it bursts into flame from the intensity of the reaction. If the vapour be passed through a tube of porcelain heated to redness, beautiful rhombohedral crystals of sesquioxide of chromium are formed: these crystals are isomor-

phous with those of corundum; they are hard enough to cut glass, and are of a very dark green colour. During their formation, oxygen and chlorine escape, in consequence of the following reaction; $2\ (CrClO_2) = Cr_2O_3 + Cl_2 + O$.

Chlorochromic acid is analogous to the chloromolybdic, chlorotungstic, and chlorosulphuric acids in composition, and in the products which it yields when decomposed. In order to prepare it, 10 parts of common salt are fused with 17 of chromate of potash; the melted mass, when cold, is broken into fragments, and gently heated in a retort with 30 parts of oil of vitriol: the chlorochromic acid distils over readily.

(658) TERFLUORIDE OF CHROMIUM ($CrF_3 = 83{\cdot}3$) is obtained by distilling 4 parts of chromate of lead, 3 of powdered fluor-spar, and 8 of strong sulphuric acid, in a platinum retort; sulphates of lead and lime are formed, and the terfluoride distils as a deep red vapour, which by a low temperature is reduced to a blood-red liquid. The reaction which attends its formation may be thus represented; $PbO,CrO_3 + 3\ CaF + 4\ (HO,SO_3) = PbO,SO_3 + 3\ (CaO,SO_3) + 4\ HO + CrF_3$. Any other chromate may be substituted for chromate of lead in this operation.

Terfluoride of chromium forms deep red fumes of chromic acid the moment that it comes into the air, as it is instantly decomposed by moisture: by conducting the vapour into a moistened platinum crucible the vessel becomes speedily filled with voluminous crystals of chromic acid; hydrofluoric acid is formed at the same time, and may be expelled from the chromic acid by a gentle heat. The action of water upon the terfluoride may be thus represented; $CrF_3 + 3\ HO = CrO_3 + 3\ HF$.

(659) NITRIDE OF CHROMIUM (Cr_3N_2?; Schrötter).—If the anhydrous sesquichloride of chromium be heated in a current of dry ammoniacal gas, chloride of ammonium sublimes, whilst the chloride of chromium is decomposed, emitting a purple light, and an insoluble chocolate-brown compound of chromium and nitrogen is left. If it be heated to between 300° and 400° in a current of oxygen, it takes fire and burns with a beautiful red light into oxide of chromium, emitting nitrogen gas mixed with red fumes of peroxide of nitrogen.

(659 *a*) SULPHATES OF CHROMIUM ($Cr_2O_3, 3\ SO_3 = 196{\cdot}5$).—There are three varieties of this salt. One of them is a *green* soluble compound, which is freely dissolved by alcohol, but does not crystallize. It may be obtained by boiling either of the hydrated oxides of chromium with sulphuric acid. A second modification, of a *violet* colour, may be procured by digesting 8 parts

of the green hydrated oxide of chromium dried at 212° with 9 parts of oil of vitriol, in a shallow vessel exposed to the air at ordinary temperatures. The mixture gradually absorbs water, and becomes converted in two or three weeks' time into a greenish-blue mass of crystals: if these crystals are dissolved in water they form a blue liquid from which alcohol separates the salt in small octohedra containing 15 Aq. This modification forms with sulphate of potash, or with sulphate of ammonia, a beautiful violet double salt (chrome alum) which crystallizes by spontaneous evaporation in bold octohedra, and corresponds in form and composition to ordinary alum, the formula of the potash-salt being ($KO,SO_3 + Cr_2O_3\ 3\ SO_3, + 24$ Aq), *sp. gr.* 1·826. The solution of the violet sulphate, when boiled, becomes green; and if the crystals of chrome alum be dissolved in water, and the solution be boiled, the plum-coloured liquid also becomes green, and loses the power of crystallizing on cooling. If the violet sulphate be heated to 212° it melts in its water of crystallization, loses 10 Aq, and becomes converted into the green salt: but if the temperature be raised to about 700°, both the green and the violet modification are rendered anhydrous, and a third salt is obtained in *red* crystals, which are no longer soluble in water, or even in concentrated acids, or aqua regia. If digested for a long time with water, however, it becomes converted into the soluble form (Schrötter, *Poggendorff's Annal.*, liii. 513). The composition of these three sulphates would be represented as follows:—

Red insoluble sulphate . . .	$Cr_2O_3, 3\ SO_3$
Green soluble sulphate . . .	$Cr_2O_3, 3\ SO_3 + 5\ HO$
Violet soluble sulphate . . .	$Cr_2O_3, 3\ SO_3 + 15\ HO$

Several subsulphates of chromium may also be formed.

NITRATE OF CHROMIUM ($Cr_2O_3, 3\ NO_5$) is a green very soluble salt; when gently ignited, it loses its acid, and yields a brown oxide of chromium (CrO_2), which is regarded as a chromate of sesquioxide of chromium (Cr_2O_3, CrO_3).

(659 *b*) OXALATES OF CHROMIUM.—Oxalate of ammonia gives a green insoluble precipitate when mixed with a solution of green sesquichloride of chromium, but if the hydrated sesquioxide of chromium be digested with oxalic acid, a green soluble oxalate is formed.

The oxalate of chromium forms two remarkable series of double salts, viz., *dark blue* salts, which form bluish-green solutions in water with the general formula ($3\ MO,Cr_2O_3, 3\ C_4O_6$), and *garnet-coloured* salts, which form cherry-red solutions in water, of the for-

mula ($MO,Cr_2O_3, 2\ C_4O_6$). The *Blue potash-salt* ($3\ KO,Cr_2O_3, 3\ C_4O_6+6\ Aq$) may be obtained by boiling 19 parts of the bichromate of potash, 23 of neutral oxalate of potash, and 55 of crystallized oxalic acid: the chromic acid is reduced to the state of sesquioxide, and carbonic acid is evolved in abundance, owing to the following reaction:—

$$2\ (KO,2\ CrO_3)+2\ (2KO,C_4O_6)+7\ (2\ HO,C_4O_6)=12\ CO_2+14\ HO$$
$$+2\ (3\ KO,Cr_2O_3, 3\ C_4O_6).$$

The solution is evaporated to dryness, redissolved in water, and set aside to crystallize. The salt is deposited in large rhombic prisms which appear to be black by reflected light; and blue by transmitted light. They appear greenish when powdered, the solution is red by transmitted and green by reflected light: ammonia does not precipitate the oxide of chromium from the solution; potash occasions no precipitate till the liquid is boiled. Corresponding salts may be obtained containing soda, ammonia, baryta, strontia, lime, and magnesia instead of potash, but these different salts vary in the proportion of water which they retain.

The *Red potash-salt* ($KO,Cr_2O_3, 2\ C_4O_6+8\ Aq$ or $12\ Aq$) may be procured by adding 55 parts of oxalic acid to a boiling concentrated solution of 19 parts of bichromate of potash, carbonic acid being expelled owing to the following decomposition:—

$$2\ (KO, 2\ CrO_3)+7\ (2\ HO,C_4O_6)=12\ CO_2+14\ HO$$
$$+2\ (KO,Cr_2O_3, 2\ C_4O_6).$$

It may be obtained by spontaneous evaporation crystallized in small rhomboidal tables, which are dark-red both by reflected and by transmitted light: the salt requires about 10 parts of cold water for solution, but is soluble to any extent in boiling water. The concentrated solution is dark-green or nearly black by reflected light, but red by transmitted light. Potash gives no precipitate in the solution till raised to ebullition; neither does ammonia cause any separation of oxide of chromium. An analogous salt may be formed with ammonia ($H_4NO,Cr_2O_3, 2\ C_4O_6+8\ Aq$).

(660) Characters of the Compounds of Chromium:—

1.—*Salts of the Protoxide* are but little known. They absorb oxygen rapidly from the air; they are sparingly soluble in water, and form either red or blue solutions, which, like those of the protosalts of iron, absorb binoxide of nitrogen in large quantity, and form dark-brown solutions. With the protosalts of chromium *potash* gives a brown precipitate of hydrated protoxide of chromium; *ammonia*, a greenish-white precipitate, which, if

hydrochlorate of ammonia be present, is redissolved by excess of ammonia, forming a blue liquid which becomes red as it absorbs oxygen. With *sulphide of potassium* they give a black sulphide; and with *ferrocyanide of potassium* a greenish-yellow precipitate. These salts reduce solutions of gold to the metallic state, and convert corrosive sublimate into calomel.

2.—The *Salts of the Sesquioxide* have a sweetish astringent taste, and are poisonous. They are either green or violet coloured; the green solutions generally transmit a red light. With *ammonia* they yield a bulky gelatinous precipitate of hydrated sesquioxide of chromium. *Potash* and *Soda* give a green precipitate, which is dissolved with a green colour in excess of the cold alkaline solution, but is re-precipitated completely by boiling the liquid. The *carbonates of the alkalies* give a green precipitate which is redissolved by an excess of the alkaline liquid. *Sulphuretted hydrogen* gives no precipitate. The *sulphides of the alkaline metals* precipitate the green sesquioxide of chromium, with escape of sulphuretted hydrogen. If any of these precipitates be fused with nitre, it yields a yellow soluble chromate of potash.

3.—*The Chromates.*—*Before the blowpipe* they colour borax and microcosmic salt green. When boiled with diluted sulphuric acid, to which a little alcohol or sugar has been added, they are decomposed, and the chromic acid is reduced to the green oxide of chromium, which is dissolved by the sulphuric acid, and is precipitated with its characteristic colour on neutralizing with ammonia. Most of the chromates are strongly coloured. Many of them are insoluble in water, but they are nearly all readily dissolved by diluted nitric acid. Their solutions give a yellow precipitate with *salts of lead*, a red with *nitrate of silver*, and an orange with *subnitrate of mercury*. When heated with oil of vitriol the chromates evolve oxygen; with hydrochloric acid they evolve chlorine. In both cases salts of the green oxide of chromium are formed.*

(661) *Estimation of Chromium, and Separation from the Alkalies and Alkaline Earths.*—Chromium may be most accurately estimated in the form of sesquioxide. It may be easily reduced to this condition, even if it exist in solution in the form of a chromate, by acidulating with hydrochloric acid, and transmitting a

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* Workmen engaged in the manufacture of bichromate of potash are liable to the gradual destruction of the nasal bones and to the occurrence of ulceration of the throat, in appearance a good deal resembling that occasioned by secondary syphilis. Small doses of corrosive sublimate have been found to act as an effectual remedy in such cases (Crace Calvert).

current of sulphuretted hydrogen: the liquid must then be boiled, and on the addition of ammonia to the hot solution the oxide of chromium is precipitated. It is to be well washed, and ignited in a covered platinum crucible; 100 parts of the anhydrous oxide contain 68·68 of chromium.

The *Separation of Chromium from the Earths, and from Zinc, Cadmium, Cobalt, Nickel, and Iron* may be effected by fusing the mineral, or the precipitate obtained by ammonia from its solution in an acid, with a mixture of carbonate of potash and nitre; the chromium is thus converted into chromic acid, and forms a soluble compound, from which the chromium may be precipitated as directed in the foregoing paragraph, whilst the earths and the other metals remain in the insoluble portion, either in the form of oxides or of carbonates.

§ VIII. Manganese ($Mn=27·5$). *Sp. Gr.* 8·013.

(662) The ores of this metal are tolerably abundant, and it enters, in greater or less quantity, into the composition of a vast number of minerals, so that it is widely diffused throughout the mineral kingdom. The most important and valuable ore of manganese is the black oxide, which occurs either massive or in radiated crystals.

Manganese was first recognised as a distinct metal by Gahn in 1774. It is reduced to the metallic state with difficulty. The best method consists in mixing the carbonate into a paste with oil and sugar, and introducing it into a crucible lined with charcoal, furnished with a cover luted on: it must at first be heated gently, to expel the volatile matters, and then ignited intensely for a couple of hours in the heat of a forge. It may thus be obtained in the form of a metallic globule which contains a variable quantity of carbon; the carbon may be removed by fusing the metal a second time in a porcelain crucible with a little carbonate of manganese. A solution of chloride of manganese also yields plates of the reduced metal when subjected to electrolysis.

Manganese is of a greyish-white colour, and is brittle, but hard enough to scratch steel; it is very feebly magnetic. By exposure to the air, it speedily becomes oxidated, and should be preserved either in sealed tubes or under naphtha.

Manganese enters into combination with both carbon and silicon when fused with them: the carbide, when treated with acids, leaves part of the carbon as a black powder: the compound of

manganese with silicon is decomposed with difficulty even by aqua regia, in which case it leaves a residue of silicic acid.

Metallic manganese is not employed as such in the arts. It yields various alloys, but none of them are of practical importance, with the exception of its combination with iron, which is harder and more elastic than iron alone. The chief uses of the compounds of manganese are chemical, the peroxide being extensively employed to decompose muriatic acid and furnish chlorine. It likewise supplies the chemist with his cheapest source of oxygen, and is employed as a colouring material in the manufacture of glass and enamels. It is also used as a flux in the preparation of cast steel; and it furnishes a useful mordant to the calico printer, when precipitated in the form of brown hydrate upon the fibre.

(663) OXIDES OF MANGANESE.—Manganese forms several compounds with oxygen. The protoxide, MnO, is a powerful base; the sesquioxide, Mn_2O_3, is feebly basic; the red oxide, a compound of these two, MnO,Mn_2O_3, is quite indifferent to the action of acids; so also is the deutoxide or black oxide, MnO_2: but the two higher oxides have well-marked acid characters. The formula for manganic acid is MnO_3, and that for permanganic acid Mn_2O_7. Neither of these acids, however, can be obtained except in combination with water or with a metallic oxide.

The *protoxide* ($MnO=35{\cdot}5$) may be obtained easily by igniting carbonate of manganese, or any of the higher oxides of the metal, in a current of hydrogen; it is of an olive-green colour, and unless it has been strongly heated, absorbs oxygen from the air; if ignited in the air it burns, and is converted into a brown superior oxide. It may be obtained as a white hydrate by decomposing a salt of manganese by any alkali, but it immediately begins to absorb oxygen from the air, and turns brown. It is soluble in ammonia, especially if the solution contain an ammoniacal salt. The protoxide unites readily with acids, forming well-characterized salts, which are of a pale rose colour; they are neutral to litmus.

Sesquioxide ($Mn_2O_3=79$); *Sp. Gr.* 4·82.—This oxide is found in its anhydrous form in acute octohedra, constituting *braunite*; it occurs naturally in a hydrated state in *manganite* (Mn_2O_3, HO; *sp. gr.* 4·35), which is of a blackish-brown colour, and forms brilliant prismatic crystals. The sesquioxide of manganese may be obtained as a brown hydrate, by passing chlorine through the carbonate of the protoxide suspended in water, and afterwards removing the excess of the carbonate by means of diluted nitric

acid. Sulphuric acid dissolves it slowly if a portion of the protoxide be present, and a deep red solution is formed; hydrochloric acid in the cold also forms a soluble compound with it: if these solutions be heated they are decomposed, and a salt of the protoxide is the result. When ignited, the sesquioxide loses one eighth of its oxygen, and leaves the red oxide. The salts of the sesquioxide are isomorphous with those of alumina and sesquioxide of iron. It appears to be the sesquioxide of manganese that imparts the violet colour to glass to which the black oxide has been added; and the colour of the amethyst is also said to be due to this oxide.

Binoxide, deutoxide, or *peroxide* (MnO, MnO_3), or ($MnO_2 = 43{\cdot}5$); *Sp. Gr.* 4·94.—This oxide is the black manganese of commerce and the *pyrolusite* of mineralogists: it is found in steel-grey rhombic prisms. *Psilomelane* is a black stalactitic or amorphous variety frequently mixed with one of the lower oxides of the metal. *Varvicite* ($Mn_2O_3, 2\,MnO_2,HO$; *Sp. Gr.* 4·53) is the name given to a hard lamellated crystalline hydrate, found by Phillips at Hartshill, in Warwickshire. *Wad* is also a hydrated peroxide of manganese, with a variable amount of water; it is in a less compact form than psilomelane, and is of a brown colour. Small quantities of cobalt and of the carbonates and nitrates of the earths are frequent constituents of these ores.

Binoxide of manganese is a good conductor of electricity, and is strongly electro-negative in the voltaic circuit. When mixed with acids it furnishes a valuable oxidizing agent. When ignited it gives off one third of its oxygen, and the red oxide is left; $3\,MnO_2 = (MnO, Mn_2O_3) + O_2$: if heated with concentrated sulphuric acid, half its oxygen escapes, and a protosulphate is formed; $MnO_2 + HO, SO_3 = MnO, SO_3 + HO + O$. With hydrochloric acid chlorine is abundantly evolved, and a protochloride of manganese is left. Nitric acid has but little effect upon it. Binoxide of manganese is procured in a hydrated form as a reddish-brown powder, when manganate or permanganate of potash is decomposed by an acid. When the red oxide is treated with nitric acid, a black hydrate of the peroxide is left, containing $4\,MnO_2, HO$. The same compound is formed on adding a solution of chloride of lime to a neutral solution of sulphate or chloride of manganese.

(664) *Commercial Assay of Oxide of Manganese.*—The commercial value of black oxide of manganese depends upon the proportion of chlorine which a given weight of it will liberate when it is heated with hydrochloric acid. This quantity of chlorine

varies much in different samples, and is dependent upon the proportion of oxygen which the oxide of manganese contains in excess of that which is necessary to its existence as protoxide. A convenient method of estimating this excess of oxygen is founded upon the circumstance that the black oxide of manganese is decomposed in the presence of oxalic acid and free sulphuric acid; protosulphate of manganese is formed, and all the excess of oxygen reacts upon the oxalic acid and converts it into carbonic acid, which passes off with effervescence. If the mixture be weighed before the decomposition is effected, and again after it has been completed, the loss will indicate the amount of carbonic acid; and from this the available amount of oxygen is readily calculated. The reaction may be traced thus: $2\ MnO_2 + 2\ (HO,SO_3) + 2\ HO, C_4O_6 = 2\ (MnO,SO_3) + 4\ CO_2 + 4\ HO$. Each equivalent of peroxide of manganese gives 2 equivalents, or almost exactly its own weight of carbonic acid.

The apparatus of Will and Fresenius (fig. 314, p. 371) is well adapted to the performance of this experiment: 100 grains of the oxide of manganese to be tested is reduced to an extremely fine powder, and mixed with 150 grains of oxalic acid; the mixture is placed in the flask, *a*, and about 1½ ounce of water is added: the experiment is then proceeded with exactly as in the method already described for estimating carbonic acid in a carbonate (481). The decomposition of the ore is known to be complete as soon as all the black particles have disappeared.

If the sample of oxide of manganese contain a carbonate of any of the earths, as may be readily ascertained by the effervescence which will be occasioned on moistening a portion of the oxide with diluted nitric acid, it will be necessary to remove this carbonate. This is easily done by washing the weighed portion in the flask itself with nitric acid diluted with from 16 to 20 parts of water; as soon as the effervescence has ceased, the acid liquid must be carefully poured off, and the flask filled up once or twice with distilled water; the oxide must be allowed to subside: in order to retain any suspended particles, the washings may be thrown upon a small filter, which is afterwards introduced into the flask, and the experiment is then proceeded with as usual.

The *Red Oxide* ($MnO, Mn_2O_3 = 114{\cdot}5$) corresponds to the black oxide of iron; it is formed by igniting any of the oxides of manganese in the open air: it occurs native in *hausmannite*, (*sp. gr.* 4·72) either massive or in four-sided pyramidal crystals of a black colour. The oxide is soluble in phosphoric and in sulphuric acid, but does not form definite salts with either of them.

(665) *Manganic Acid* ($HO,MnO_3=9+51{\cdot}5$).—When equal weights of caustic potash and finely levigated peroxide of manganese are fused together, a substance is formed, which, when dissolved in a small quantity of water, has a green colour, but which, when largely diluted, becomes purple, and ultimately claret-coloured, whilst a precipitate of hydrated binoxide of manganese is deposited. This substance has, owing to these changes of colour, been long known under the name of *mineral chameleon.* The colouring material is manganic acid, which, when in combination with potash, has a green colour: it is an unstable compound, and readily either parts with oxygen, or absorbs a larger amount of it, in the latter case forming a red compound; and hence these changes of colour are produced.

Manganic acid undergoes rapid spontaneous decomposition unless it be in combination with some powerful base. Such a compound may be procured by heating finely powdered peroxide of manganese with its own weight of hydrate of potash, of soda, or of baryta. Béchamp heats an intimate mixture of 10 parts of finely powdered oxide of manganese with 12 of hydrate of potash, dries it in an iron dish, and heats the porous residue to dull redness in an earthen retort, into the tubulure of which a green glass tube is luted; he then transmits a current of pure dry oxygen as long as it is absorbed. If the green mass thus obtained be treated with a small quantity of cold water, it is partially dissolved, forming a green solution, from which the manganate of the base may be crystallized by evaporating it *in vacuo* over sulphuric acid. These crystals are isomorphous with the corresponding sulphates and chromates. Manganate of potash (KO, MnO_3) is anhydrous, and readily soluble in water. Manganic acid has a very intense colouring power: this fact enables manganese in very minute quantity to be detected before the blowpipe; the material supposed to contain it is fused upon platinum foil with a little carbonate of potash or of soda: if any trace of manganese be present, a green colour is imparted to the fused mass.

The *manganates* are very unstable; they are decomposed by boiling their solutions. In the solid form they are readily decomposed by elevation of temperature, and oxygen is evolved; an excess of potash renders the salt more stable: organic matter also readily abstracts oxygen from them. Their solutions must not even be filtered through paper. Sulphurous and phosphorous acids readily reduce the manganates to a salt of protoxide of man-

ganese; sulphurous acid and manganate of potash, for example, produce the following result:—

$$KO,MnO_3 + 2\ SO_2 = MnO,SO_3 + KO,SO_3.$$

(666) *Permanganic Acid* ($HO,Mn_2O_7 = 9 + 111$).—If a solution of manganate of potash be largely diluted with water, the colour changes from green to violet; the manganic acid passes to a higher state of oxidation, and permanganate of potash is formed.

This salt may be prepared by mixing intimately 4 parts of finely powdered peroxide of manganese with $3\frac{1}{2}$ parts of chlorate of potash; 5 parts of hydrate of potash are dissolved in a small quantity of water, and added to the mixture, which is dried and reduced to powder, and then heated to dull redness for an hour in an earthen crucible (Gregory). When cold, the mass is treated with water, and filtered through a funnel plugged with asbestos; the solution, after being neutralized with sulphuric acid, on evaporation yields beautiful red acicular crystals of permanganate of potash (KO,Mn_2O_7). If a solution of manganate, prepared by Béchamp's process, be decomposed by transmitting a current of carbonic acid until the green colour has been converted into red, very fine crystals of the permanganate are obtained on evaporating the clear liquid after decantation from the precipitated oxide of manganese. The crystals of the permanganate are isomorphous with those of perchlorate of potash; they require about 16 parts of cold water for solution.

Permanganate of potash is in certain cases a useful oxidizing agent: it may be employed to detect the occurrence of sulphurous acid in solution in sulphuric or in hydrochloric acid; sulphurous acid quickly deoxidizes it and destroys its colour if present. Neutral solutions of the sulphides and the pentathionates quickly discharge the colour of a solution of permanganate of potash, and a similar effect is produced by acid solutions of the sulphites, hyposulphites, tetrathionates, sulphocyanides, and nitrites. The trithionates produce the same effect, but more slowly. Acidulated solutions of the protosalts of iron and of tin, of the suboxide of mercury, of teroxide of antimony, and acid solutions of arsenious acid, likewise decolorize a solution of permanganate rapidly. A solution of this salt constitutes a test-liquid which may be very usefully employed in many cases of volumetric analysis, as already exemplified in the instance of the ores of iron (651).

The *permanganates* are much more stable than the manganates; their solutions may be boiled without undergoing decomposition. Organic matter, however, combines with part of the

oxygen contained in the acid, and reduces it first to manganic acid and then to the binoxide of the metal, which is precipitated in flocculi as a hydrate: their solutions, therefore, must not be filtered through paper, but through a funnel loosely plugged with asbestos. When ignited, oxygen is given off, and a manganate is reproduced, which, if the heat be too great, is in turn decomposed with a further extrication of oxygen. Most of the permanganates are freely soluble in water; the permanganate of silver is the least soluble of these salts. If concentrated solutions of permanganate of potash and of nitrate of silver be mixed together, a red crystalline permanganate of silver is deposited. It may be employed for the preparation of the other permanganates; if it be levigated with water, and mixed with a solution of the chloride of the metal of which the permanganate is required, double decomposition occurs, and chloride of silver is formed, whilst the desired permanganate is obtained in solution. In this way the permanganate of baryta may be procured, and from it the permanganic acid may be obtained in solution, by the cautious addition of diluted sulphuric acid, so long as any precipitate is produced: on evaporation it may be obtained as a brown partially crystalline mass, which is very soluble in water: its solution is decomposed by mere elevation of the temperature; at a little beyond 100° F. hydrated peroxide of manganese is deposited, and oxygen gas escapes.

(667) *Protosulphide of Manganese* ($MnS + x\,Aq$) is obtained as a yellowish-red hydrate, by precipitating a salt of the protoxide by hydrosulphate of ammonia. The presence of traces of iron, cobalt, or nickel renders it black: it speedily becomes oxidized by exposure to the air. A crystalline sulphide may be obtained in black rhombic prisms, by heating the hydrated sesquioxide in the vapour of bisulphide of carbon. A native sulphide of manganese is occasionally met with, as *manganese blende,* of a brownish-black or steel-grey colour, and feeble metallic lustre. The other sulphides of manganese have not been accurately examined.

(668) CHLORIDES OF MANGANESE.—Three chlorides of this metal may be obtained: a protochloride, a sesquichloride, and a perchloride (Mn_2Cl_7): but there is some doubt as to the composition of the latter compound.

Protochloride of Manganese ($MnCl + 4\,Aq = 63 + 36$).—This substance is obtained abundantly as a waste product in the preparation of chlorine, by acting on the black oxide of the metal: the chlorine escapes, and the chloride of manganese is dissolved. If this solution be evaporated to dryness, redissolved in water, and about one fourth of its bulk be precipitated by means of carbonate

of soda, an impure carbonate of manganese is obtained. If this precipitate, after it has been well washed, is boiled with the remainder of the solution, the whole of the iron will be precipitated in the form of peroxide, while oxide of manganese takes its place, and carbonic acid is expelled, leaving a solution of chloride of manganese freed from all metallic impurities except cobalt and nickel. A still better process consists in concentrating a solution of the crude chloride by evaporation, to expel the excess of acid, and afterwards diluting with water. A current of sulphuretted hydrogen is transmitted, by which the iron is reduced to the state of protoxide; the manganese may then be obtained free from iron, nickel, and cobalt by suspending freshly precipitated sulphide of manganese in water, and adding it to the liquid as long as the fresh portions of sulphide become blackened; the manganese displaces the other metals from their solution, and they are precipitated as black hydrated sulphides: for example, $FeCl + HO,MnS = MnCl + HO, FeS$. On evaporation the chloride of manganese crystallizes in a tabular form with 4 Aq. It is of a delicate pink colour and slightly deliquescent; by heat an anhydrous chloride may be procured, which is soluble in alcohol, and crystallizes with two equivalents of alcohol.

A *sesquichloride* may be obtained in solution by acting on the sesquioxide of manganese with cold hydrochloric acid: it is of a dark brown colour: it must be concentrated by evaporation *in vacuo*.

The *Perchloride* Mn_2Cl_7? (Dumas) is obtained by dissolving permanganate of potash in oil of vitriol and adding fused chloride of sodium in small portions at a time: it is a greenish-yellow gas, which condenses at 0° F. to a greenish-brown liquid. The fumes in a moist air assume a purple colour from the formation of permanganic acid: water decomposes it instantly, forming a red solution of permanganic and hydrochloric acids. It is probable that this compound is an oxychloride of the metal, somewhat analogous to chlorochromic acid (657).

Fluorides of manganese, corresponding to each of these chlorides, have been formed.

(669) Sulphate of Manganese ($MnO,SO_3 + 5\ Aq = 75{\cdot}5 + 45$) is obtained for the use of the calico printer, by digesting the binoxide in diluted sulphuric acid, in order to remove the carbonates, then heating the oxide with oil of vitriol, evaporating to dryness, and gently igniting the residue to decompose the sulphate of iron, which does not resist so high a temperature as the sulphate of manganese. On digesting the mass, after it has become

cool, in water, the sulphate of manganese is dissolved, and may be obtained in crystals by evaporation: it crystallizes below 42° with 7 Aq; between 45° and 68° with 5 Aq; and between 68° and 86° with 4 Aq (Brandes). It forms a double salt with sulphate of potash ($MnO,SO_3+KO,SO_3+6\,Aq$), which is isomorphous with the corresponding double sulphate of magnesia.

The sesquisulphate of manganese cannot be obtained in crystals, but it forms a double salt with sulphate of potash, which crystallizes in octohedra ($KO,SO_3+Mn_2O_3,3\,SO_3+24\,Aq$), and corresponds in form and composition with common alum.

CARBONATE OF MANGANESE ($MnO,CO_2=57{\cdot}5$).—The anhydrous carbonate forms the native *Manganese spar*, and frequently accompanies spathic iron: the artificial carbonate may be obtained as a white hydrate, $2\,(MnO,CO_2)+HO$, on precipitating the chloride by a carbonate of one of the alkalies: it becomes brownish by drying.

(670) CHARACTERS OF THE SALTS OF MANGANESE.—The salts of the *protoxide* are the only salts of manganese of importance: they are of a delicate rose colour, and have an astringent taste. With *potash* and with *soda* their solutions yield a white precipitate of hydrated protoxide, which absorbs oxygen rapidly, and becomes brown by exposure to the air. *Ammonia* gives a similar precipitate, which is soluble in excess of the ammoniacal liquid, especially when it contains chloride of ammonium; the solution absorbs oxygen quickly, and deposits a brown hydrated peroxide of manganese. The *carbonates of the alkalies* give a white precipitate of carbonate of manganese, soluble in chloride of ammonium. With *hydrosulphate of ammonia* a characteristic flesh-coloured hydrated sulphide of manganese is formed, which becomes brown by exposure to air. *Sulphuretted hydrogen* gives no precipitate in the solutions of manganese; but a neutral solution of acetate of manganese is partially precipitated by this gas. *Ferrocyanide of potassium* gives in neutral solutions a white precipitate soluble in acids; in neutral solutions *ferridcyanide of potassium* produces a brown precipitate. Mr. Crum has pointed out an extremely delicate test of the presence of manganese in the reaction which occurs if a compound of manganese be mixed with diluted nitric acid, and a little peroxide of lead be added: on boiling the mixture, the red colour of permanganic acid is produced by a trace of manganese which is too small to be otherwise recognised. *Before the blowpipe*, when fused on platinum wire or foil, with a little carbonate of soda, the compounds of manganese give a very cha-

racteristic bluish-green opaque bead: a bead of borax or of microcosmic salt becomes violet in the oxidizing flame, if manganese be present; the colour disappears in the reducing flame.

(671) *Estimation of Manganese, and Separation from the Alkalies.*—Manganese is generally estimated in analysis in the form of the red oxide of manganese, which contains 72·7 per cent. of the metal. For this purpose it is precipitated from a boiling solution of its salts by carbonate of potash or of soda; the precipitated carbonate is well washed and then heated to redness, by which carbonic acid is expelled, and the red oxide is produced by absorption of oxygen from the air.

Separation of Manganese from the Alkaline Earths.—The solution must be rendered nearly neutral, and hydrosulphate of ammonia added, which precipitates the manganese as sulphide: the sulphide must then be redissolved in hydrochloric acid, precipitated by carbonate of potash, and the manganese estimated, after ignition, as red oxide. It is however apt to retain some portions of the earths when thus separated. The oxide must therefore be again redissolved in hydrochloric acid; chloride of ammonium must be added, and then a mixture of ammonia and carbonate of ammonia in excess, by which the manganese will be held in solution; but if lime, baryta, or strontia be present, the earths will remain undissolved in the form of carbonates, which must be collected on a filter, weighed, and deducted from the weight of the oxide previously obtained.

Separation from Zinc, Cadmium, Cobalt, and Nickel.—The solution is mixed with acetate of potash in excess to convert the metals into acetate, then sulphuretted hydrogen is transmitted; the manganese remains in solution, whilst the other metals are precipitated as sulphides if the solution is only faintly acid.

If cadmium alone is present, the addition of acetate of potash is unnecessary.

Separation from Iron, Chromium, Uranium, Aluminum, and Glucinum.—This is readily effected after converting the iron into a persalt and diluting the solution largely with water, by digesting it upon finely levigated carbonate of baryta. Manganese alone remains in the liquid, the other oxides being displaced by baryta. The excess of baryta is removed by sulphuric acid, and the manganese precipitated by carbonate of soda.

Manganese is connected by isomorphous relations with a great number of the elementary bodies. Its protoxide is isomorphous with the magnesian group: its sesquioxide is isomorphous with alumina and the sesquioxides of iron and chromium. The manganates are isomorphous with the sulphates, and the permanga-

nates with the perchlorates. It does not, however, hence follow that 1 atom of metallic manganese is isomorphous with 1 atom of magnesium, of aluminum, or of sulphur; and that 2 atoms of the metal are isomorphous with 1 atom of chlorine, of bromine, or iodine: because we know that metallic zinc is not isomorphous with iron, although their salts are usually considered to be isomorphous.

CHAPTER XV.

GROUP V.—CERTAIN METALS WHICH FORM ACIDS WITH OXYGEN.

§ I. TIN ($Sn=59$). *Sp. Gr.* 7·292.

(672) THIS beautiful metal is one of those which have been longest known to man, as it is mentioned in the Books of Moses. Tin, however, is met with in but few localities. Its only ore of importance is the deutoxide, or tin-stone, which occurs crystallized in prisms, isomorphous with those of titanic acid. It is usually found in veins, running through primitive rocks of porphyry, granite, or clay-slate, and is generally mingled with the sulphides and arsenides of copper and iron, and frequently also with wolfram. The most celebrated tin mines are those of Cornwall, which were worked before the Roman invasion; they furnish annually upwards of 6000 tons of the metal. The mines of Malacca also yield a very pure tin: the metal is likewise obtained to a smaller extent from Mexico. The tin veins in Cornwall are frequently associated with those of copper, and they run almost invariably east and west. The tin ore is often met with in alluvial soils, whither it has been carried from its original position by the action of water. In this case the ore occurs in detached, rounded masses, and is very pure, constituting what is termed *stream tin*. The position of the veins is frequently traced by following the stream towards its source, up to the point where the ore ceases to be found; a careful examination of the vicinity generally leads to the discovery of the vein.

(673) *Extraction of Metallic Tin.*—In order to extract the metal from the ore, it is subjected to a series of operations, some of which are of a mechanical, and others of a chemical character. They may be classified thus:—

1.—*Stamping and Washing*, to remove the earthy and lighter

portions. 2.—*Roasting*, to decompose the pyrites and get rid of the arsenic and sulphur. 3.—*Washing*, to dissolve out sulphate of copper, and carry off the oxide of iron. 4.—*Reduction*, by which the tin is separated from the oxygen and the *gangue*, or earthy matter. 5.—*Refining*, or liquation, and *boiling* with green wood.

1.—The purer portions of the ore are first picked out by hand; the residue, consisting chiefly of tin-stone, with the earthy impurities of the matrix, mixed with arsenical copper and iron pyrites, passes to the stamping mill, where it is reduced to a coarse powder. This powder is then buddled and washed, to remove the lighter impurities.

2.—The heavier portion, however, still retains a considerable quantity of arsenical iron and copper pyrites. The next operation is intended to get rid of these substances; with this view the washed ore is roasted in a reverberatory furnace until the arsenic and a good deal of the sulphur are expelled, and the ore becomes converted into yellowish-brown powder; this process usually lasts about twelve hours. During this roasting, frequent stirring is necessary in order to expose fresh surfaces freely to the air. By this means the iron pyrites is decomposed, and is converted into sulphurous acid and peroxide of iron; the arsenic is expelled as arsenious acid, and the greater part of the sulphide of copper is converted into sulphate of copper; this conversion is completed by exposing the mass in a moistened state to the air for some days.

3.—The sulphate of copper is then dissolved out by lixiviation; after which the principal part of the peroxide of iron, as it is much lighter than the oxide of tin, is got rid of by washing.

4.— The washed ore is now ready for reduction.* In order to attain this object it is mixed with from one fifth to one eighth its weight of powdered anthracite or of charcoal, and with a small proportion of lime to facilitate the fusion of the siliceous gangue, which still remains mingled with the ore. The mixture having been rendered damp, for the purpose of preventing the finer particles from being carried away by the current of air, is introduced into the reducing furnace. This is a reverberatory furnace with a low arch or crown. The charge having been placed upon the hearth, the doors are closed up and the heat is gradually raised for five or

* When much wolfram is contained in the ore it is sometimes fused with carbonate of soda before proceeding to the reduction; the tungstic acid is thus removed in the form of tungstate of soda, which is extracted by water, and is sometimes employed in calico printing as a mordant; it has lately also been applied to muslin dresses, to prevent them from burning with flame, should they happen to take fire.

six hours; the binoxide of tin is thus reduced by the carbon, before the temperature rises high enough to cause the oxide to fuse with the silica, with which it would form an enamel difficult of reduction. Towards the end of the operation the heat is raised until it becomes very intense; the slags are thus rendered fluid, and the reduced metal subsides to the bottom, and is allowed to run off into cast iron pans, from which it is ladled off into moulds; but the ingots thus obtained are by no means pure.

5.—They are therefore next submitted to a process of *liquation*, which consists in heating the ingots to incipient fusion, upon the bed of a reverberatory furnace: the purer tin, being the more fusible portion, gradually melts out and leaves an alloy, which has a higher melting point. This less fusible portion when remelted forms the inferior variety called *block tin*. The tin which has run out of the ingots is drawn off into a second pan in which the metal is gently heated, being kept in a state of fusion by a fire underneath; here it is agitated briskly by thrusting into the mass stakes soaked in water; the steam thus produced as it bubbles up through the molten metal, carries the dust, slag, and other mechanical impurities to the surface. After this treatment has been continued for about three hours the metal is allowed to remain undisturbed for a couple of hours; it is then skimmed, ladled out, and cast into ingots for the market. The portion contained in the upper half of the pan is the purest, as owing to the low density of tin, and its tendency to separate from its alloys, it rises to the surface. The finest quality of the metal is frequently heated a second time to a temperature a little short of its melting point; at this high temperature it becomes brittle, and, if allowed to fall from a height, it breaks into irregular prismatic fragments, which are known as *dropped* or *grain tin*. The splitting of the mass into these fragments is a rude guarantee of the purity of the metal, since impure tin does not become brittle in this manner.

On the continent the stream tin is frequently reduced in small blast furnaces termed by the French *fourneaux à manche*; the fuel used in this case is charcoal. The tin which is imported from Banca is almost chemically pure. English tin usually contains small quantities of arsenic, copper, iron, and lead, and often traces of gold.

When required in a state of perfect purity, the metal may be obtained by means of voltaic action. For this purpose a concentrated solution of crude tin in hydrochloric acid is placed in a beaker, and water is cautiously poured in without disturbing

the dense solution below. If a bar of tin be plunged into the liquid, beautiful prismatic crystals of pure tin are gradually deposited on the bar at the point of junction between the metallic solution and the water.

(674) *Properties.*—Tin is a white metal with a tinge of yellow, and a high metallic lustre. It is rather soft, and is very malleable, but is deficient in tenacity. At a temperature of about 212° its ductility is considerable, and it may then be easily drawn into wire. In a laminated state it is well known as *tinfoil.* If a bar of tin be bent, it emits a creaking sound, a property which it possesses in common with cadmium; if bent several times in succession backwards and forwards, it becomes sensibly hot at the point of flexure. These effects depend upon a mechanical alteration of the relative position of its molecules, and their mutual friction. Tin, when handled, communicates a peculiar odour to the fingers. It is a tolerably good conductor both of heat and electricity. It fuses at 442°, according to Crichton (or 451°, Person), but is not sensibly volatilized in the furnace. It may be obtained in crystals by slow cooling after fusion. Tin is but slowly tarnished by exposure to the air and moisture at ordinary temperatures, but if exposed to the air at a high temperature it becomes rapidly converted into the binoxide and burns with a brilliant white light. Nitric acid of sp. gr. 1·3 acts upon it violently, and produces an insoluble hydrated binoxide of the metal known as metastannic acid; at the same time, owing to the decomposition of water, a considerable quantity of ammonia is formed, which enters into combination with the excess of acid. Strong hydrochloric acid, when heated upon tin, dissolves it gradually with extrication of hydrogen. Aqua regia, if not too concentrated, dissolves the metal and converts it into the bichloride. Diluted sulphuric acid is without action on the metal in the cold; but if the concentrated acid be boiled upon it, the tin becomes converted into sulphate, while sulphurous acid escapes. The hydrates of potash and soda act upon tin at high temperatures, hydrogen being evolved, whilst a soluble metastannate of the alkali is formed.

Owing to its brilliancy, and its power of resisting ordinary atmospheric changes, tin is largely employed as a coating upon other more abundant, but more oxidizable metals, to protect them during use. Iron and copper are especially adapted to the operation of tinning. In India, tin is applied instead of silver to steel and iron articles by way of ornament; the tin is melted, and while still liquid is agitated in a box till it has become solid; the fine powder thus procured is separated, by suspension in water, from the

coarser particles, and is made into a thin paste with glue; it is then applied in the desired pattern; when perfectly dry it is burnished, and afterwards varnished; its brilliancy is thus preserved unchanged.

(675) *Tin Plate.*—The ordinary process of tinning iron differs from the foregoing one, and is far more important in its economical results. In tin plate an actual alloy of the two metals is formed upon the surface of the iron, the external surface being pure tin. For the manufacture of tin plate, the best charcoal iron is required. After the iron has been rolled and cut into sheets of suitable thickness and size, its surface is made chemically clean. For this purpose the sheets are immersed for four or five minutes in a mixture of sulphuric acid and water; after which they are raised to a red heat in a reverberatory furnace; they are then withdrawn, allowed to cool, and hammered flat. In order to detach from them all the scales of oxide, they are passed between polished rollers, and as they emerge they are plunged one by one into a mixture of bran and water which has become sour by exposure to the air; here they remain for some hours, and are thence transferred to a vessel containing a mixture of diluted sulphuric and hydrochloric acids; lastly, they are scoured with bran, and plunged into pure water or lime-water, where, if the surface be clean on immersion, they may remain for any length of time without rusting: these preliminary steps are necessary in order to secure a clean surface, as the tin will not adhere to an oxidated or even a dusty plate. In some works the plates, after they have been scoured, are further cleaned with hydrochloric acid holding zinc in solution, and then dipped into the melted tin in the manner about to be described.

The plates having been prepared by either of the foregoing processes are next plunged one by one into a large vessel of melted tallow free from salt, and after remaining there for an hour they are immersed in the bath of melted tin, which is preserved from oxidation by a stratum of grease three or four inches thick. Here they remain for about an hour and a half, they are then withdrawn and allowed to drain. After this they are plunged into a second bath of pure tin, and the excess of tin is removed by again heating them in a bath of tallow: the tin melts and runs down to the lower edge of the plate; when cool, this thickened margin is finally reduced by dipping the edge of the plate once more into tin kept at a temperature much above its melting-point; the heat quickly fuses the superfluous metal, which is then detached by giving the plate a sharp blow. Tin plate is sometimes made to exhibit a beauti-

ful crystalline appearance, known under the term *moirée métallique*. A mixture of 2 parts of nitric acid, with 2 of hydrochloric acid, is made with 4 of water: the tin plate is gently heated, and the liquid spread evenly over with a sponge; the crystals gradually appear. The plate is then plunged into water, dried quickly, and varnished. Different coloured varnishes are used to vary the effects.

Tinning of copper is the same in principle, but is a simpler operation than the tinning of iron; the surface of the metal is rendered clean by rubbing it while heated with sal ammoniac; when quite bright the copper is sprinkled with a little rosin to prevent oxidation, and melted tin is then poured on and spread over the surface with tow by the workman, who keeps the article constantly at a high temperature; the superfluous tin is wiped off with the tow. The addition to the tin of one fourth of its weight of lead renders the operation more easy, as the alloy is more perfectly liquefied. Pins, which are made of brass wire, are tinned by boiling them for a few minutes with a solution containing 1 part of cream of tartar, 2 parts of alum, and 2 of common salt in 12 parts of water, with a quantity of granulated tin: in the course of a few minutes a brilliant, white, closely adhering coat of tin is deposited upon the surface of the pins.

(676) *The alloys of tin* which are employed in the arts are numerous. *Britannia Metal* is one which is a good deal used for making teapots and spoons of a low price; it consists of equal parts of brass, tin, antimony, and bismuth. *Pewter* is another alloy of this description; both of these possess considerable malleability, pewter being intermediate in hardness between lead and Britannia metal. The best pewter consists of 4 parts of tin, and 1 of lead. Another alloy, which is intermediate in properties between pewter and Britannia metal, is called *Queen's metal;* it is used for the manufacture of teapots and common spoons. It consists of 9 parts of tin, 1 part of antimony, 1 of bismuth, and 1 of lead. *Plumbers' solder* is an alloy of tin and lead which is more fusible than pure lead: *fine solder* consists of 2 parts tin and 1 of lead; *common solder* of equal parts of lead and tin; and *coarse solder* is composed of 2 of lead to 1 of tin. Tin and zinc form a hard, white alloy; if the two metals be fused together in equal proportions, the resulting compound is nearly as tough as brass.

Tin forms several important alloys with copper. *Speculum metal*, used for the mirrors of reflecting telescopes, consists of 1 part tin and 2 copper, or ($SnCu_4$): it is of a steel-white colour, extremely hard, brittle, and susceptible of a high polish. The

proportions of the constituents of speculum metal recommended by different authorities vary, and sometimes a small quantity of arsenic is added to the alloy. *Bell metal* consists of about 78 of copper and 22 of tin, or (CuSn). *Gun metal* contains only 9 or 10 per cent. of tin. *Bronze* contains less tin, with usually an addition of 3 or 4 per cent. of zinc. Bronze admits of a peculiar kind of tempering. If it be annealed, and allowed to cool slowly, it becomes hard, brittle, and elastic; but if cooled suddenly, it may be hammered, and worked at the lathe; this property is taken advantage of in the manufacture of articles with this alloy; they are wrought in the soft state, and are afterwards hardened by annealing. The effect of sudden cooling upon bronze is therefore just the reverse of that which is produced by it upon steel. These alloys of copper and tin are much harder than copper itself, and considerably more fusible. The melting point of copper, according to Daniell, is 1996°; but an alloy of tin and copper containing 6·6 per cent. of tin, fused at 1690°; and one with 12·3 per cent. of tin, at 1534° F. These alloys have a specific gravity greater than the mean of that of the metals which enter into their composition. They resist oxidation in the air more completely than copper.

An inconvenience in the use of the alloys of copper and tin arises from the circumstance, that, when melted, the two metals, owing to their difference in density, have a tendency to separate from each other, even after they have been well incorporated: the tin accumulates in the upper portions of the melted mass, where it forms a more fusible alloy. It is therefore very difficult in large castings to obtain a mass of metal the composition of which is uniform throughout.

The *Amalgam of Tin and Mercury* is employed for the silvering of mirrors. In order to apply it to the glass, a sheet of tinfoil is spread evenly upon a smooth slab of stone, which forms the top of a table carefully levelled, and surrounded by a groove, for the reception of the superfluous mercury. Clean mercury is poured upon the tinfoil, and spread uniformly over it with a roll of flannel; more mercury is then poured on until it forms a fluid layer of the thickness of about half-a-crown; the surface is cleared of impurities by passing a linen cloth lightly over it; the plate of glass is carefully dried, and its edge being made to dip below the surface of the mercury, is pushed forward cautiously; all bubbles of air are thus excluded as it glides over and adheres to the surface of the amalgam. Weights are then placed upon the glass, and the stone is gently inclined so as to allow the excess of mer-

cury to drain off; the plate is then covered with flannel, and loaded with weights for 24 hours, at the end of which time it is placed upon a wooden table, the inclination of which is increased from day to day until the mirror assumes a vertical position: in about a month it is sufficiently drained to allow the mirror to be framed. The amalgam usually contains about 4 parts of tin to 1 part of mercury.

Several of the compounds of tin are employed in the arts. The binoxide is used to some extent in the preparation of enamels, and both the chlorides of tin are substances of great importance to the dyer and the calico printer.

(677) Oxides of Tin.—With oxygen, tin forms two principal compounds, the protoxide and the binoxide, besides some intermediate oxides of minor importance.

Protoxide of Tin ($SnO=67$) is obtained as a white hydrate, (SnO,HO), by pouring a solution of the protochloride of the metal into one of carbonate of soda or potash in excess; the carbonic acid escapes with effervescence. When moist, this hydrate absorbs oxygen from the air, but not when dry. By ignition in closed vessels filled with nitrogen or with carbonic acid it becomes anhydrous. The anhydrous protoxide may also be obtained by decomposing the protoxalate of tin by heat, in closed vessels. If heated in the open air it glows, and is converted into the binoxide. If the hydrated oxide be boiled with a solution of potash in excess, it is dissolved, and in a few days metallic tin is separated, peroxide of the metal remaining in solution. If boiled with a weak solution of potash, in quantity insufficient to dissolve the oxide, it becomes anhydrous, and is converted into a mass of black crystalline needles; these needles when heated decrepitate powerfully, increase in bulk, and are converted into an olive-brown powder. By evaporating down a solution of sal ammoniac containing hydrated oxide of tin in suspension until the sal ammoniac begins to crystallize, the oxide of tin becomes anhydrous and assumes a brilliant scarlet colour, which however by friction disappears, and becomes brown. The hydrated oxide is readily dissolved by acids, but the anhydrous oxide is more slowly acted upon by them.

(678) *Binoxide of Tin* ($SnO_2=75$; *Sp. Gr.* 6·95) occurs native in the anhydrous form, and constitutes the only ore of tin that is worked. 100 parts of it contain 78·66 of the metal. It is met with crystallized in square prisms, which are hard enough to scratch glass; they have usually a brown colour, owing to the presence of peroxide of iron or of manganese. It is insoluble in

acids, but if heated with an alkali, it enters into combination with it, and forms a soluble compound.

In its hydrated condition binoxide of tin has the characters of an acid, and forms two remarkable varieties, which have been termed respectively metastannic and stannic acids (Fremy, *Ann. de Chimie*, III. xxiii. 393). Like the metaphosphoric and phosphoric acids, they require each a different amount of base for saturation, the stannic acid combining with the greatest proportion of base.

Metastannic Acid ($HO,Sn_5O_{10}+4$ Aq) is readily procured by treating metallic tin with nitric acid; violent action, attended with extrication of nitrous fumes, occurs, and the tin is converted into a white, crystalline, insoluble mass, which is hydrated metastannic acid; after washing it with cold water, the acid, when dried in air, consists of Sn_5O_{10},10 HO (Fremy). In this state it reddens litmus paper; when dried at 212° it loses half its water, and by ignition becomes anhydrous, and of a pale buff colour: in this form it possesses the properties of the native oxide, and constitutes the *putty powder* employed for polishing plate; it is also largely used for giving whiteness and opacity to enamels.

In its hydrated condition metastannic acid is insoluble in nitric acid; concentrated sulphuric acid, when heated with it, dissolves it freely and forms a compound soluble both in water and in alcohol; by boiling the solution it is decomposed, and the two acids are separated. Hydrochloric acid combines with it, but does not dissolve it; the compound is soluble in pure water, but is reprecipitated on the addition of acid in excess, or on boiling the solution. Metastannic acid is freely soluble in solutions of potash and of soda, as well as in solutions of their carbonates, but it is not dissolved by ammonia, unless recently precipitated from a cold solution of its salts by the addition of an acid; the precipitate is not soluble in ammonia after it has been boiled. The metastannates are not crystallizable, and are precipitated by adding caustic potash to their aqueous solution; the granular precipitate may be drained upon a tile, and dried at 260°. The potash salt has a strongly alkaline reaction; it consists of ($KO,Sn_5O_{10}+4$ Aq). The metastannates of the alkalies can only exist in the hydrated condition; if strongly heated they are decomposed and become insoluble; when the residue, after ignition, is treated with water, metastannic acid is left, whilst the alkali is dissolved. Metastannic acid may be recognised by the beautiful golden-yellow colour which it yields when its hydrate is moistened with protochloride of tin, owing to the formation of metastannate of tin ($SnO,Sn_5O_{10}+4$ Aq). The only metastannates which are soluble are those of potash and soda;

they are precipitated in the gelatinous state from their solutions by the addition of almost any of the neutral salts of soda, potash, or ammonia.

(679) *Stannic Acid* (HO,SnO_2).—This variety of the hydrated oxide of tin may be procured by precipitating a solution of bichloride of tin by ammonia, or still better by adding to the solution of the bichloride a quantity of an insoluble carbonate, such as chalk or carbonate of baryta, insufficient for its entire decomposition; it is thus separated as a gelatinous precipitate, which may be readily washed clean: when dried *in vacuo*, the composition of the hydrate is (HO,SnO_2). In this state it is freely soluble in hydrochloric acid, with which it reproduces bichloride of tin; it is also soluble even in diluted sulphuric acid, but the stannic acid is separated on boiling. Nitric acid dissolves it freely. Stannic acid is soluble in the cold in solutions of potash and of soda, but not in ammonia; by a heat of 284° it is converted into metastannic acid. In combination with the alkalies it forms compounds which crystallize readily, especially from solutions which contain an excess of alkali. Their general formula is MO,SnO_2.

The soluble stannates have a powerfully alkaline reaction; they absorb carbonic acid from the air when in solution, and are precipitated by solutions of most of the salts of potash, soda, and ammonia.

Stannate of Potash ($KO,SnO_2 + 4\,Aq$) is easily prepared by heating any form of peroxide of tin with excess of caustic potash; on dissolving and evaporating the product, transparent oblique rhombic prisms are formed. When heated to redness, the stannate of potash may be rendered anhydrous. *Stannate of Soda* ($NaO,SnO_2 + 4\,Aq$) may be prepared in the same way as the stannate of potash. It crystallizes with facility in six-sided tables, when a solution saturated at about 100° F. is heated to the boiling point, as it is more soluble in cold than in hot water. This stannate is now largely prepared as a mordant for the use of the dyer and calico-printer. It forms the basis of what is technically known as *tin-prepare liquor*. Copper is quickly tinned by a solution of this salt.

Stannate of the Protoxide of Tin, or *Sesquioxide of Tin* as it was formerly called (SnO,SnO_2), may be prepared as a slimy grey hydrate, soluble in ammonia, by boiling pure hydrated sesquioxide of iron with a solution of protochloride of tin; protochloride of iron remains in solution, $2\,SnCl + Fe_2O_3 = 2\,FeCl + SnO,SnO_2$. It is soluble in ammonia and also in hydrochloric acid; the latter solution gives a purple precipitate with salts of gold.

(680) The SULPHIDES OF TIN are three in number,—the protosulphide, the bisulphide, and the sesquisulphide: the latter is unimportant.

The *Protosulphide* ($SnS=75$) may be procured by fusing the metal with sulphur, when it forms a bluish-grey crystalline mass, easily dissolved by melted tin; it may also be obtained by passing sulphuretted hydrogen through a protosalt of tin in solution, when it falls as a chocolate-brown hydrate. It is soluble in bisulphide of ammonium, and in the sulphides of the alkaline metals, if they contain an excess of sulphur. Protosulphide of tin combines with the sulphides of the electro-negative metals, such as arsenic and antimony. Hydrochloric acid dissolves it with extrication of sulphuretted hydrogen.

The *Sesquisulphide* (Sn_2S_3) may be prepared by mixing the protosulphide with one third of its weight of sulphur, and heating to dull redness; it is only partially soluble in hydrochloric acid.

The *Bisulphide of Tin* ($SnS_2=91$) is known as *Mosaic gold;* it forms a beautiful yellow flaky compound, which is obtained by preparing an amalgam of 12 parts of tin and 6 of mercury: this is reduced to powder and mixed with 7 parts of sublimed sulphur and 6 of sal ammoniac. This mixture is introduced into a flask with a long neck, and is heated gently so long as any smell of sulphuretted hydrogen is perceptible; the temperature is then raised to low redness; calomel and cinnabar are sublimed, and a scaly mass of bisulphide of tin remains. If the heat be pushed too far, part of the sulphur is expelled, and the operation fails: the sal ammoniac appears by its volatilization to moderate the heat produced during the sulphuration of the tin, which would otherwise rise so high as to decompose the bisulphide. Bisulphide of tin is used in the arts to imitate bronze. Aqua regia is the only acid that decomposes it, but it is readily soluble in the alkalies. A hydrated bisulphide of tin, of a dingy yellow, is produced by passing sulphuretted hydrogen through a solution of the persalts of tin. This hydrate is readily dissolved by hydrosulphate of ammonia, evolving sulphuretted hydrogen: it is also soluble in the alkalies, and in hot hydrochloric acid. With sulphide of sodium it forms a salt which may be obtained in yellow crystals consisting of $2\,NaS,SnS_2+12\,Aq$.

The bisulphide fuses when chlorine is passed over it; 6 equivalents of the gas are absorbed, without the aid of heat, and a yellow crystalline compound is obtained which may be considered as a combination of 1 atom of bichloride of tin with 2 atoms of bichloride of sulphur, $SnCl_2, 2\,SCl_2$.

(681) CHLORIDES OF TIN.—Tin forms with chlorine two compounds, SnCl, and $SnCl_2$, which correspond in composition with the sulphides of the metal.

Protochloride of Tin (SnCl=94·5).—The hydrate of this salt may be obtained by dissolving tin in hydrochloric acid. This solution is usually effected on the large scale in copper vessels, since the voltaic opposition of the two metals favours the solution of the tin: on evaporating the liquid till it crystallizes, prismatic needles are formed (SnCl + 2 Aq; *Sp. Gr.* 2·759); by a heat of 212° it may be rendered anhydrous, but it generally loses a portion of hydrochloric acid at the same time. The protochloride is decomposed if mixed with a large quantity of water, hydrochloric acid remains in solution, and a white, hydrated oxychloride (SnCl, SnO + 2 Aq) subsides. When exposed to the air, in crystals or in solution, the protochloride absorbs oxygen and forms a mixture of bichloride and oxychloride of tin. Protochloride of tin has a strong affinity both for chlorine and for oxygen; it therefore acts as a powerful reducing agent. Thus it deoxidizes completely the salts of mercury, of silver, and of gold. Advantage is sometimes taken of this circumstance in the analytical determination of the quantity of mercury, since all the salts of mercury, when boiled with the protochloride of tin, are decomposed, and yield their mercury in a metallic form. Sulphurous acid is likewise deprived by it of its oxygen, producing a yellow precipitate of bisulphide of tin when mixed with a solution of the salt. Protochloride of tin reduces the metallic acids in the salts of chromic, tungstic, molybdic, arsenic, antimonic, and manganic acids to a lower state of oxidation; it also converts the persalts of iron into protosalts, and the protosalts of copper into salts of the red oxide. Protochloride of tin is extensively employed as a mordant by the dyer and calico-printer, under the name of *salts of tin*, and they also use it for deoxidizing indigo and the peroxides of iron and manganese.* It forms double chlorides with many of the chlorides of the metals of the alkalies and alkaline earths; these double salts are capable of crystallization.

The anhydrous protochloride or *butter of tin* may be procured by distilling a mixture of equal weights of tin filings and corrosive

* The proportion of protochloride of tin available for this purpose in any sample may be determined by Penny's method:—A solution of a weighed quantity of the protochloride in hydrochloric acid is taken, and a standard solution of bichromate of potash is added until a drop of the liquid when mixed with acetate of lead gives a yellow precipitate, showing that the chromic acid is no longer reduced; the reaction may be thus indicated:—

$$3\,SnCl + KO, 2\,CrO_3 + 7\,HCl = 3\,SnCl_2 + KCl + Cr_2Cl_3 + 7\,HO.$$

sublimate; $HgCl + Sn = SnCl + Hg$: it remains behind as a grey brilliant mass with a vitreous fracture; at a full red heat it may be distilled. On passing a current of chlorine over it, heat and light are evolved, and the bichloride of tin is formed.

(682) *Bichloride of Tin* ($SnCl_2 = 130$); *Sp. Gr. of vapour*, 9·2; *of liquid*, 2·367 at 32°; *Boiling pt.* 239°·5.—This compound may be prepared either by passing dry chlorine over melted tin, or by mixing 4 parts of corrosive sublimate with 1 part of tin filings: on the application of heat a colourless liquid distils; $2\,HgCl + Sn$ yielding $SnCl_2 + 2\,Hg$. It emits dense white fumes when exposed to the air: when mixed with water, intense heat is evolved, and a hydrate is formed; this compound crystallizes in rhombohedra ($SnCl_2 + 2\,Aq$), when it is allowed to form spontaneously, by attracting moisture from the air: but though freely soluble in a small quantity of water, copious dilution causes the precipitation of hydrated stannic acid, and hydrochloric acid is set free. Bichloride of tin is readily soluble in water acidulated with hydrochloric acid. When its aqueous solution is mixed with a solution of the sulphate of one of the alkalies, hydrated binoxide of tin is precipitated; $SnCl_2 + 4\,HO + 4\,(NaO,SO_3)$ becoming $SnO_2, 2\,HO + 2\,NaCl + 2\,(NaO,HO, 2\,SO_3)$, bisulphate of the alkali remaining in solution.

The bichloride of tin forms numerous double salts with the soluble chlorides; the compound with chloride of potassium crystallizes in anhydrous octohedra, $KCl,SnCl_2$; a similar constitution holds in the corresponding ammoniacal salt ($H_4NCl,SnCl_2$), which is the *pink salt* of the dyer. An impure bichloride of tin is largely used by the dyers under the name of nitromuriate of tin, or *composition*; it is generally prepared by dissolving tin at a gentle heat in a mixture of nitric acid and sal ammoniac.

The other salts of tin are unimportant.

(683) Characters of the Salts of Tin.—Tin forms two series of salts, the salts of the protoxide and the salts of the binoxide: the bichloride of tin is the only salt of the latter class that has been minutely examined.

1.—The *Protosalts of Tin* are nearly colourless; with the exception of the chloride, they are not often prepared: they have a powerfully astringent taste; when in solution they absorb oxygen rapidly from the air; when largely diluted with water the solution becomes milky, but it is rendered clear by a small excess of hydrochloric acid. The *fixed alkalies* produce a white precipitate of hydrated protoxide of tin, which is soluble in excess of the alkali,

but on boiling, part of the oxide is deposited as a black crystalline powder. *Ammonia* gives a white hydrated oxide of tin, but the precipitate is not redissolved by an excess of ammonia. The *carbonates of the alkalies* give a similar precipitate, whilst carbonic acid escapes with effervescence. A very characteristic reaction is the production, with *sulphuretted hydrogen,* of a chocolate-brown precipitate of hydrated protosulphide of tin. With *sulphide of ammonium,* a similar precipitate is formed, which is soluble in the sulphides of the alkaline metals. With a dilute solution of *chloride of gold,* they give, if used in excess, a brown precipitate of reduced gold; in smaller quantity, they yield a beautiful purple precipitate, the purple of Cassius. *Ferrocyanide of potassium* gives a white precipitate, soluble in hydrochloric acid.

2.—The *Persalts of Tin** are found to give with the *caustic alkalies* a white precipitate, soluble in excess of the alkalies, and this solution yields no precipitate when it is boiled. *Carbonates of the alkalies* give a white hydrated oxide with escape of carbonic acid: the precipitate is insoluble in excess of the alkaline salt. *Sulphuretted hydrogen* and *hydrosulphate of ammonia* both produce a dirty yellow precipitate of hydrated sulphide of tin, which is soluble in excess of the sulphides of the alkaline metals, and in the caustic alkalies.

All the compounds of tin *before the blowpipe* with soda on charcoal in the reducing flame, give white malleable globules of the reduced metal.

(684) *Estimation of Tin, and Separation from the foregoing Metals.*—Tin is estimated in the form of the anhydrous binoxide; 100 parts of which contain 78·66 of the metal.

The separation of tin from all the metals hitherto described, with the exception of cadmium, is effected by means of sulphuretted hydrogen, which precipitates none of these metals from their solutions in the mineral acids. The mixed sulphides of tin and cadmium may be at once evaporated to dryness with nitric acid: on treating the residue with water, nitrate of cadmium will be dissolved, and the insoluble oxide of tin will remain. The sulphide of cadmium is also easily separated from the sulphides of tin by hydrosulphate of ammonia, which dissolves the sulphides of tin and leaves the sulphide of cadmium. Both the sulphides of tin, by ignition in a current of air, are gradually converted into the binoxide of tin: this change may be accelerated by moistening them with nitric acid.

Tin may also be separated from all metals with the exception

* The presence of tartaric acid in some cases interferes with these reactions.

of antimony, arsenic (and lead if sulphuric acid be present), by evaporating the solution nearly to dryness with nitric acid, and washing the residue with water strongly acidulated with nitric acid. The tin remains as metastannic acid, and by ignition furnishes the anhydrous binoxide.

§ II. Titanium ($Ti=25$).

(685) Titanium is a comparatively rare metal, which presents considerable analogy with tin. It was discovered by Gregor as a constituent of menaccanite in the year 1791. Its principal ores are titaniferous iron, and rutile, anatase, and brookite, which are three different forms of titanic acid, coloured by variable quantities of the oxides of iron, manganese, and chromium. When titanic acid is intensely heated with charcoal, it is reduced, but is not fused. A remarkable compound of the metal is frequently found, in the form of copper-coloured cubic crystals, adhering to the slags of the Welsh and other iron furnaces. These crystals are hard enough to scratch agate; they have a specific gravity of 5·3. No acid, except a mixture of nitric and hydrofluoric acids, has any action upon them, but they are oxidized by fusion with nitre, or by ignition in a current of oxygen: they are volatile at an extremely high temperature. These crystals were supposed by Wollaston to be metallic titanium, but Wöhler showed that they consist of a combination of cyanide with nitride of titanium; they contain 18 per cent. of nitrogen, and 4 of carbon, having a formula ($TiCy, 3\ Ti_3N$). Another nitride of the metal (Ti_3N_2), also formerly mistaken for metallic titanium, is procured in copper-coloured scales by igniting the ammonio-chloride of titanium ($2\ H_3N,TiCl$) in closed vessels, in a current of ammonia.* If a current of dry ammoniacal gas be transmitted over powdered titanic acid, heated to redness in a porcelain tube, a violet-coloured nitride of titanium (TiN) is formed. So strong, indeed, is the affinity of titanium for nitrogen at a high temperature, that if a mixture of titanic acid and charcoal, both in a minute state of division, be heated to whiteness, and submitted to a current of nitrogen, the whole of the nitrogen is rapidly absorbed, whilst carbonic oxide escapes, and copper-coloured crystals, having the same composition as those obtained from the blast furnace, are formed (Deville and Wöhler).

Pure titanium may be obtained by decomposing the double

* The ammonio-chloride of columbium yields a similar nitride when treated in like manner: the same remark applies also to molybdenum.

fluoride of titanium and potassium, with potassium in a tube filled with pure hydrogen, and through which a current of pure hydrogen is maintained. It then forms a grey, amorphous powder, which burns in air with scintillation, and deflagrates in oxygen with dazzling brilliancy. It may also be obtained in prismatic crystals by heating sodium in the vapour of bichloride of titanium. The metal is soluble in hydrochloric acid with evolution of hydrogen, forming a colourless solution, from which ammonia precipitates a black hydrated protoxide.

(686) Three Oxides of Titanium probably exist—the protoxide, the sesquioxide, and the binoxide, or titanic acid.

The *Protoxide* ($TiO=33$) has not been obtained in a pure state. It appears to be formed when titanic acid is heated in a crucible lined with charcoal: but where the acid is actually in contact with the charcoal, a film of metallic titanium, mixed with a portion of nitride, is obtained. The protoxide is a black powder nearly insoluble in acids, and is gradually oxidized by exposure to a high temperature in air, or by fusion with nitre.

If a solution of titanic acid in hydrochloric acid be digested with zinc, a purple, hydrated *sesquioxide* or titanate of titanium (TiO,TiO_2) is deposited, which absorbs oxygen from the air with great rapidity, becoming white from the formation of titanic acid. Hydrochloric acid dissolves it sparingly, and forms a blue solution.

Titanic Acid ($TiO_2=41$).—This compound occurs in *menaccanite* and *iserine* as titanate of iron; but more commonly it is met with in the uncombined condition, as titanic anhydride, constituting the principal ore of the metal. It is found native under three distinct crystalline forms, each of which has a different specific gravity. Of these, the densest and most abundant is *rutile* (sp. gr. 4·25): it occurs in long striated prisms or needles of a brown colour, isomorphous with those of tin-stone. The second variety, *brookite* (sp. gr. 4·13), is found in right rhombic prisms, sometimes opaque, at others transparent, and of a pale brown; whilst the third variety, *anatase* (sp. gr. 3·9), is found at Dauphiny in acute octohedra, which are semi-transparent and of a yellowish-brown or blue colour. Corresponding differences are observed in the titanic anhydride artificially prepared in the laboratory. Like the binoxide of tin, it may, when hydrated, be obtained in two isomeric forms, possessed of different properties. In fact, the existence of two dissimilar modifications is a very usual occurrence in the case of metallic oxides possessed of feeble acid powers.

Pure titanic acid may be obtained by reducing rutile to a

fine powder, and fusing it with thrice its weight of carbonate of potash. On treating the mass with hot water, an impure bititanate of potash remains. It is dissolved in hydrochloric acid, next mixed with an excess of ammonia, and the precipitate is digested in hydrosulphate of ammonia, by which the tin, iron, and manganese are converted into sulphides, whilst the titanic acid remains unchanged: a solution of sulphurous acid then dissolves the sulphides, and a pure white hydrate of titanic acid is left. The water may be expelled by heat, and by long-continued ignition the colour of the compound deepens, its specific gravity increasing till it acquires a density equal to that of rutile. In this state it is insoluble either in solutions of the alkalies, or in acids, except hydrofluoric acid and boiling oil of vitriol. This anhydride may, however, be brought into solution by heating it with a fixed alkaline carbonate, dissolving the residue with cold hydrochloric acid, and precipitating the titanic acid by means of carbonate of ammonia: it then forms a white gelatinous hydrate, which dries into a semitransparent mass capable of reddening litmus. The liquid long remains turbid; it cannot be rendered clear by filtration, unless an excess of some ammoniacal salt be present. Hydrated titanic acid is dissolved by solutions of the alkalies, and it yields definite salts with them. When fused with potash it forms a transparent yellowish glass. The hydrate of titanic acid is soluble in diluted hydrochloric acid; it is also dissolved by sulphuric acid, and forms a definite sulphate (TiO_2, SO_3), which may be evaporated to dryness at a low temperature without undergoing decomposition. Both these acid solutions are decomposed by boiling them, and the insoluble variety of titanic acid is precipitated. When the soluble hydrate is heated, it loses water and becomes insoluble. It becomes yellow on ignition, but recovers its whiteness on cooling. When fused with bisulphate of potash, titanic acid is dissolved, and may be obtained in solution by adding water; it may thus be distinguished and separated from silica, which is not dissolved by this means.

(687) A *Bisulphide of Titanium* (TiS_2) may be obtained in green scales; it is not soluble in the sulphides of the alkaline metals.

Bichloride of Titanium ($TiCl_2=96$; *Sp. Gr. of vapour*, 6·836, *of liquid*, 1·761 *at* 32°; *Boiling point*, 277°) is a fuming volatile liquid, resembling the bichloride of tin. It may be obtained by decomposing pure titanic acid, intimately mixed with charcoal, and heated to redness in a porcelain tube, by means of a current of dry chlorine gas. It is a colourless liquid, which combines with

a small quantity of water to form a crystallizable compound. A large quantity of water produces its decomposition, hydrated titanic acid being separated. Deville obtained square prisms of metallic titanium by decomposing the vapour of the bichloride with sodium.

(688) CHARACTERS OF THE COMPOUNDS OF TITANIUM.—1.—The *salts of the protoxide* are but little known; with the *carbonates of the alkalies* they give a blue precipitate, which becomes first brown and ultimately green.

2.—The *titanates* of the alkalies are of a yellowish-white colour: the normal salts are insoluble in cold water; hot water removes the alkali, while most of the titanic acid remains undissolved. Hydrochloric acid dissolves them, forming a solution which, when boiled, becomes turbid from deposition of titanic acid; *ammonia,* when added to this solution, produces a white precipitate. *Infusion of galls* produces an orange-coloured precipitate in the acid solutions of the titanates; a precipitate of similar colour is produced by *ferrocyanide of potassium.* In the reducing flame of *the blowpipe* the titanates give with microcosmic salt a beautiful purple or bluish glass, which becomes colourless in the oxidizing flame. This reaction distinguishes the titanates from the tantalates.

(689) *Estimation of Titanium.*—Titanium is always estimated in the form of titanic acid. Its solution in cold hydrochloric acid is not precipitated by sulphuretted hydrogen, by which means it may be separated from tin and cadmium, both of which are thrown down from the acid as insoluble sulphides. The solution is next mixed with tartaric acid, and supersaturated with hydrosulphate of ammonia: iron, nickel, cobalt, manganese, and zinc are thus separated in the form of sulphides. The solution is then evaporated to dryness, and the carbon is burned off; titanic acid is left, mixed with the salts of the earths and alkalies contained in the mixture; the residue is fused with potash, redissolved in the cold with hydrochloric acid, and on boiling the liquid, to which a little diluted sulphuric acid has been added, the titanic acid is precipitated. This process, however, is not very accurate; indeed the exact determination of the quantity of titanium in its compounds is a matter of considerable difficulty.

§ III. Columbium—Tantalum.

(690) Columbium, or Niobium ($Nb=48\cdot8$) was discovered in the year 1801 by Hatchett, who found it in a black mineral from Massachusetts, termed columbite. In the following year Ekeberg obtained a new metal, which he termed *Tantalum* ($Ta=68\cdot8$), from the tantalite and yttro-tantalite of Sweden.

These two metals were asserted by Wollaston to be identical—an opinion generally received until Rose showed that the American mineral contained a metallic acid different from that furnished by the tantalite: this acid he termed the *Niobic;* and its metallic constituent, niobium, is the columbium of Hatchett. Rose at the same time stated that associated with this was a second metallic acid, which he termed the *Pelopic,* but which he has since ascertained to be a compound of the metal which he called niobium.

Columbium and tantalum have been but incompletely studied; they are too rare to need a detailed description here: they have a considerable analogy with silicon,—tantalic acid, according to Rose, having the formula TaO_2.

Hermann supposed the yttro-tantalite of Siberia to contain a new metal, analogous to columbium, to which he gave the name of *Ilmenium;* but he has since proved the so-called ilmenic acid to be a mixture of the tantalic and columbic acids.

§ IV. Molybdenum ($Mo=48$). *Sp. Gr.* 8·615 to 8·636.

(691) The principal ore of molybdenum is the bisulphide, a mineral in appearance much resembling plumbago, and which occurs chiefly in Bohemia and in Sweden. Molybdenum is also occasionally found oxidized, in combination with oxide of lead, as molybdate of lead. The metal may be obtained by roasting the pure native sulphide in a free current of air; the sulphur passes off as sulphurous acid, whilst the molybdenum also combines with oxygen, and remains behind in the form of molybdic acid. If this be mixed into a paste with oil and charcoal, and exposed to the heat of a smith's forge, in a crucible lined with charcoal, it is reduced to the metallic state. In this form molybdenum is white, brittle, and very difficult of fusion. The acid may also be reduced by heating it to redness in a porcelain tube in a current of hydrogen: when the pulverulent metal is heated in the open air it is gradually oxidized, and finally converted into molybdic acid. It is readily oxidized by nitric acid; if the metal be in excess, a soluble nitrate of the binoxide is obtained; if the acid predomi-

nate, the oxidation proceeds further, and molybdic acid is formed: aqua regia produces similar results. Molybdenum is also oxidized when fused with nitre, and molybdate of potash is produced.

(691 *a*) OXIDES OF MOLYBDENUM.—Molybdenum forms three oxides; the protoxide (MoO), and the binoxide (MoO_2) are both possessed of basic characters: the third (MoO_3) is a powerful metallic acid.

The *protoxide* (MoO=56) is precipitated from the solution of a molybdate in hydrochloric acid which has been reduced by means of a bar of zinc, on adding ammonia in excess; it is thus thrown down as a black hydrate which absorbs oxygen from the air: it is soluble in a solution of carbonate of ammonia, but not in those of the fixed alkalies or their carbonates. It may also be obtained in the anhydrous form, by digesting molybdic acid with zinc and hydrochloric acid.

The *binoxide* (MoO_2=64) may be prepared by igniting a mixture of 2 parts of molybdate of soda and 1 part of sal ammoniac, and digesting the mass in solution of potash, to remove any undecomposed molybdic acid. The residue when well washed is the pure oxide, which has been reduced from molybdic acid by the hydrogen of the ammonia. It is of a dark brown colour, but it becomes purple if exposed to solar light; it is nearly insoluble in acids. The hydrated binoxide may be obtained by digesting molybdic acid, mixed with copper filings, in hydrochloric acid; an excess of ammonia precipitates the oxide of a rusty-brown colour, whilst the copper is retained in solution. Hydrated binoxide of molybdenum is soluble in pure water, but is precipitated by the addition of any salt. The solution gelatinizes on keeping. The salts which this oxide forms with acids are of a reddish-brown colour, or, if anhydrous, are nearly black.

If a solution of bichloride of molybdenum be added, drop by drop, to a concentrated solution of bimolybdate of ammonia, a deep blue precipitate of molybdate of molybdenum ($MoO_2,4MoO_3$) takes place. This compound is soluble in water, but is precipitated by the addition of any saline body. The addition of a small quantity of a protosalt of tin to a soluble molybdate reduces the molybdic acid, and produces this beautiful blue compound, which may serve as a test of the presence of molybdic acid: care must be taken not to add the tin salt in excess. Another compound of the binoxide of molybdenum with molybdic acid (MoO_2, 2 MoO_3) has a green colour.

(692) *Molybdic Acid* (MoO_3=72) is obtained in the form of an impure anhydride by roasting the sulphide of molybdenum at a

low red heat; it remains behind as a dirty yellow powder; caustic ammonia dissolves the acid, leaving oxide of iron and other impurities. The ammoniacal solution crystallizes on evaporation, and by a low red heat the ammonia is expelled, leaving the anhydride behind, of a pale buff colour. It contains 66·6 per cent. of the metal and 33·4 of oxygen. The anhydride reddens moistened litmus paper, and is sparingly soluble in water, forming a yellow solution. At a red heat it fuses to a straw-coloured glass of sp. gr. 3·49: it undergoes volatilization in open vessels, and is deposited on cool surfaces in brilliant transparent needles. No definite hydrate of molybdic acid is known. When precipitated from its salts by the addition of an acid, it may be redissolved, if the acid be added in excess: with concentrated sulphuric acid it forms a blue solution. It is also freely soluble in a solution of cream of tartar. Molybdic acid unites with bases, and forms well characterized salts, both normal and acid. Those of the alkalies are soluble. Normal *molybdate of ammonia* crystallizes in colourless square prisms. An *acid molybdate of ammonia* ($2\,H_4NO, 3\,HO, 5\,MoO_3$) crystallizes readily in six-sided prisms. Other acid molybdates of the alkalies have been formed, which contain as many as 3, 4, and even 5 equivalents of the acid to 1 of fixed base. Molybdate of lead (PbO,MoO_3) occurs native in crystals of a yellow colour; it is soluble in nitric acid, and in solution of potash if the alkali be in large excess.

A solution of molybdate of ammonia may be advantageously employed in certain cases to detect the presence of very small quantities of phosphoric acid in solution. The solution suspected to contain the phosphate must be acidulated with nitric acid, and the molybdate then added. The liquid becomes yellow, and on boiling deposits a yellow crystalline precipitate, consisting of molybdic and phosphoric acids in combination with ammonia. According to Sonnenschein it contains 6·747 per cent. of ammonia, and about 3 per cent. of phosphoric acid. Arsenic acid forms a similar compound with molybdate of ammonia when the solutions are boiled.

Sonnenschein takes advantage of the insolubility of the phosphoric compound to detect small quantities of ammonia by its means. In order to prepare the test solution, he first procures the yellow precipitate, by adding molybdate of ammonia to an acidulated solution of phosphate of soda, ignites the precipitate to expel the ammonia, adds nitric acid to the residue, in order completely to reoxidize any reduced molybdic acid, evaporates to dryness, and expels the nitric acid by ignition. A solution of carbonate of soda

is employed to dissolve the remaining mixture of phosphoric and molybdic acids, and the solution is supersaturated with hydrochloric acid. This liquid, it is stated, will easily detect the presence of 1 part of sal ammoniac in 10,000 of water. Salts of soda are not affected by it, but strong solutions of the salts of potash yield a similar yellow precipitate.

(693) SULPHIDES OF MOLYBDENUM.—Three sulphides of molybdenum are known, MoS_2, MoS_3, and MoS_4: the last two are sulphur acids.

Bisulphide of Molybdenum ($MoS_2=80$; *Sp. Gr.* 4·138).—This sulphide is the principal ore of the metal: it is a soft solid of a leaden-grey colour and metallic lustre. The bisulphide may also be formed artificially by heating molybdic acid in the vapour of sulphur. It is unchanged by heat in closed vessels, but if roasted in the open air, sulphurous acid is formed and is volatilized, while molybdic acid remains. Nitric acid decomposes it, and converts the metal into molybdic acid; oil of vitriol also decomposes it when boiled upon it, forming a blue solution, whilst sulphurous acid escapes. 100 parts of this sulphide contain 60 of molybdenum and 40 of sulphur.

The *Tersulphide* ($MoS_3=96$) is precipitated by transmitting sulphuretted hydrogen through a solution of a molybdate, and adding hydrochloric acid. It is of a dark brown colour, and forms sulphur salts with the sulphides of the alkaline metals. The potash salt crystallizes in magnificent iridescent crystals (KS,MoS_3). The *quadrisulphide* of molybdenum also combines readily with the sulphides of the alkaline metals.

A *Protochloride of Molybdenum* ($MoCl=83·5$) is obtained by dissolving the protoxide in hydrochloric acid. A *bichloride* ($MoCl_2$) is procured by heating the metal in a current of dry chlorine; it forms a red vapour, which sublimes in deliquescent fusible crystals, in appearance resembling those of iodine. It may also be obtained in solution by dissolving the binoxide in hydrochloric acid.

A *Chloromolybdic Acid* sublimes in yellowish scales when the binoxide is heated in a current of chlorine. It is soluble both in water and in alcohol, and consists of ($MoCl_3$, 2 MoO_3), or (MoO_2Cl). Similar compounds may be formed with many acidifiable metals, such, for example, as tungsten, chromium, and vanadium.

(694) CHARACTERS OF THE SALTS OF MOLYBDENUM:—

1.—Little is known of the *protosalts* of molybdenum. They yield a dark brown precipitate with the *alkalies* and their car-

bonates; the precipitate is soluble in excess of carbonate of ammonia, and is deposited again on boiling the liquid; *sulphuretted hydrogen* slowly produces a brown precipitate of hydrated sulphide which is soluble in hydrosulphate of ammonia.

2.—The salts of the *binoxide* have a dark colour, and a metallic astringent taste. *Infusion of galls* produces with them a brownish-yellow solution; *ferrocyanide of potassium* gives a dark brown precipitate; *ammonia* a rusty-brown precipitate of the binoxide.

3.—The *molybdates* yield characteristic reactions with zinc, tin, and copper. With *zinc*, in dilute acid solutions, the liquid becomes first blue, then green, and finally black, after which the addition of ammonia produces a deposit of protoxide of molybdenum. The addition of a small quantity of *protochloride of tin* in solution to a liquid containing a molybdate, produces a beautiful blue molybdate of molybdenum ($MoO_2, 4\,MoO_3$), but care must be taken not to have the tin salt in excess, or the precipitate becomes dull green. *Copper filings* in similar solutions reduce the molybdic acid to the binoxide, which is precipitated as a brown hydrate by ammonia. *Before the blowpipe*, the compounds of molybdenum yield, in the oxidating flame, a colourless bead with borax, and with microcosmic salt; in the reducing flame they give a brownish-red bead with borax, and a green one with microcosmic salt.

Molybdenum is usually estimated in the form of the bisulphide, of which 100 parts contain 60 of the metal.

§ V. Tungsten ($W=92$). *Sp. Gr.* 17·6.

(695) Tungsten is a metal found in small quantities, in the form of an acid combined with lime, in the mineral known as *Scheelite*, or tungstate of lime (CaO,WO_3): or else in *wolfram* as a tungstate of iron and manganese [$MnO,WO_3, 3\,FeO,WO_3$]. It is easily obtained from the tungstate of lime, by digesting the powdered mineral in hydrochloric acid, which combines with and dissolves the lime, but leaves the insoluble tungstic acid behind: from this compound the metal itself is procured, by heating it to bright redness in a current of hydrogen gas. It is thus left of a dark grey colour, but it assumes a metallic lustre under the burnisher. If the acid be made into a paste with oil, and heated intensely in a crucible lined with charcoal for some hours, tungsten is obtained as a heavy, iron-grey metal, which is very hard and difficult of fusion. It may be heated in the air whilst in the compact state without sensible change, but in the pulverulent form it burns easily into tungstic acid. Aqua regia and nitric acid convert it

into tungstic acid, and the same change is produced by heating it in contact with the alkalies or with nitre. Pulverulent tungsten is also oxidized and dissolved by boiling it in a solution of the alkalies or of their carbonates. When tungsten is alloyed in the proportion of 9 or 10 parts with 90 of steel, it yields a metallic mass of extraordinary hardness.

(696) OXIDES OF TUNGSTEN.—Two of these are known, viz., a binoxide, which does not form salts with acids, and an acid teroxide.

The *Binoxide* (WO_2) is obtained as a brown powder by heating tungstic acid to low redness in a stream of hydrogen; or in copper-coloured scales by adding tungstic acid to dilute hydrochloric acid in which some pieces of zinc have been placed. In the latter form it attracts oxygen rapidly from the air, and is dissolved by a solution of potash, with evolution of hydrogen and formation of tungstate of potash. Wöhler obtains the binoxide from wolfram by fusing 1 part of this mineral with 2 parts of carbonate of potash: the melted mass is treated with boiling water, filtered, and mixed with a solution of $1\frac{1}{3}$ part of chloride of ammonium. The solution is then evaporated to dryness and the residue ignited; upon treating the mass with boiling water, the oxide of tungsten remains as a heavy black powder, which must be washed, first with a weak solution of potash, and afterwards with water. In this operation the hydrogen of the ammoniacal salt partially reduces the tungstic acid of the mineral.

With soda, the oxide of tungsten forms a remarkable compound of a yellow colour and metallic lustre, containing $NaO, 2\,WO_2$ (Wöhler), or, according to Wright, ($NaO,WO_2, 2\,WO_3$). It crystallizes in cubes, and is not acted upon by any acid or mixture of acids except the hydrofluoric; the solutions of the alkalies are equally without effect upon it: if heated in the air it is decomposed and partially converted into tungstate of soda. It is obtained by heating the bitungstate of soda in hydrogen gas: in order to remove the undecomposed tungstate of soda and free tungstic acid, the residue is treated in succession with water, hydrochloric acid and potash; finally it is washed with water.

Tungstic Acid ($WO_3 = 116$; *Sp. Gr.* 6·12).—Laurent considered that there were not fewer than six modifications of this acid, each of which formed a distinct class of salts; but the subsequent researches of Riche (*Ann. de Chimie*, III. l. 5) appear to have shown that there are but two modifications in addition to the anhydrides. These two different acids he terms the tungstic (HO,WO_3), and the *metatungstic* acid (HO,W_2O_6).

Tungstic anhydride may be obtained from tungstate of lime by the process already described, or by decomposing wolfram with aqua regia, evaporating to dryness, and dissolving the liberated tungstic acid in ammonia; the tungstate of ammonia is purified by crystallization, and when heated in open vessels loses its ammonia, and is converted into pure tungstic anhydride. This compound is a straw-yellow, tasteless, insoluble powder, which assumes a deeper orange tint when heated, the colour fading again as the temperature falls. In this form it is insoluble in acids, but is readily soluble in alkaline solutions; and when heated with solutions of the alkaline carbonates, it decomposes them with effervescence.

Hydrated Tungstic Acid (HO,WO_3) is obtained in the form of a yellow powder by adding hydrochloric acid in excess to a boiling solution of the anhydrous acid in any of the alkalies. The modification of acid thus obtained forms two classes of salts, one of which is normal, the other acid in composition. Even the normal salts all redden litmus faintly. When mixed in the cold with an excess of hydrochloric acid, they are decomposed, and a white sparingly soluble hydrate of tungstic acid ($WO_3,2\,HO$) is deposited.

Tungstate of Potash (KO,WO_3+Aq) is obtained by heating a strong solution of carbonate of potash to nearly its boiling point and adding tungstic anhydride so long as it produces an effervescence; crystals of the tungstate are deposited from the solution as it cools; they must be redissolved in the smallest possible quantity of boiling water, and allowed to recrystallize; this salt is soluble in about half its weight of cold water. When pure it is not decomposed by the addition of a solution of bicarbonate of soda, but if silicic acid be present, a precipitate is occasioned by this test. *Bitungstate of Potash* ($KO,2\,WO_3$) may be obtained either by fusing an equivalent of the foregoing salt with one of tungstic anhydride, or by adding a second equivalent of tungstic anhydride to a hot solution of an equivalent of the normal salt. A sparingly soluble bitungstate ($KO,2\,WO_3+3\,HO$) is obtained by transmitting a current of carbonic acid through a solution of the normal tungstate: it is deposited in pearly scales. Corresponding salts of soda may be obtained. The normal tungstate ($NaO,WO_3+2\,Aq$) crystallizes readily in rhomboidal plates. The bitungstate ($NaO,2WO_3+4\,HO$) may also be obtained in crystals. *Tungstate of ammonia* is easily obtained by digesting the acid in excess of ammonia: it crystallizes in needles at ordinary temperatures with the formula ($H_4NO,3\,HO,4\,WO_3+3\,Aq$). If crystallized at about

100° F. it contains 2 instead of 3 Aq, and the crystals, which are deposited at 212°, contain only 1 Aq, the basic water remaining unaffected. A *tungstate of tungsten* (WO_2,WO_3), of a splendid blue colour, somewhat analogous to the molybdate of the molybdenum, may be obtained by a partial reduction of tungstic acid, either by hydrogen gas, or by strongly igniting the tungstate of ammonia in closed vessels, or by digesting tungstic anhydride with zinc and hydrochloric or sulphuric acid.*

The most important native ore of tungsten is *wolfram*, which occurs in hard prismatic crystals of a dark brown colour; it is regarded as a mixture, in variable proportions, of tungstates of the protoxides of iron and manganese. Its specific gravity is very high, being about 7·3. It was this circumstance that gave rise to the name *tung-sten*, the term being a combination of two Swedish words, implying 'heavy stone.' This mineral is decomposed when boiled with hydrochloric acid, or with aqua regia, the tungstic acid remaining undissolved. It is also readily decomposed by fusion with nitre or with carbonate of soda, and a soluble tungstate of the alkali is formed.

Metatungstic Acid (HO,W_2O_6).—The salts of this acid exert an alkaline reaction upon reddened litmus, and crystallize generally with facility. They pass readily when in solution into the salts of tungstic acid: the change is gradual in neutral solutions at ordinary temperatures, more rapid in boiling liquids, or on the addition of a powerful acid, and the conversion is instantaneous if the hot liquid is mixed with an alkali or alkaline carbonate in excess. The metatungstates are always prepared by the action of hydrated tungstic acid upon the tungstates. If the white hydrated acid (WO_3, 2 HO) obtained by the action of hydrochloric acid in the cold upon the soluble tungstates be neutralized by bases, it furnishes salts which are identical with the ordinary tungstates; but if one of the soluble normal tungstates, such as the tungstate of potash, be boiled with the white hydrate of the acid in the proportion of an equivalent of each until the solution no longer becomes turbid on the addition of an acid, a new salt, the *metatungstate of potash* (KO,W_2O_6) is formed, and is deposited in small transparent prisms, as the concentrated solution cools. It is per-

* Tungstate of soda has been found to answer admirably as a preservative of muslins, &c., from burning with flame. Versmann and Oppenheim (*Pharm. Journal*, Feb. 1860, p. 426) recommend that a concentrated solution of normal tungstate of soda should be prepared, then diluted with water till of sp. gr. 1·140, after which 3 per cent. of phosphate of soda is to be added. The finished goods are dipped into the solution and dried by a hydro-extractor.

manent in the air, and very soluble in water. A metatungstate of of soda may be obtained in like manner. Two metatungstates of ammonia ($H_4NO,HO, 2\,W_2O_6+3\,Aq$) and ($H_4NO, 2\,HO, 3W_2O_6+10\,Aq$) may be also procured. The metatungstates, when mixed with nitric acid, do not at once yield a precipitate of the metallic acid.

(697) SULPHIDES OF TUNGSTEN.—There are two sulphides of this metal, the bisulphide and the tersulphide.

The *bisulphide* (WS_2) was obtained by Riche in a pure form by heating, in a covered clay crucible, an intimate mixture of equal parts of bitungstate of potash and sulphur. After fusion at a very high temperature for half an hour, the mass is poured out, powdered, and washed with boiling water. The bisulphide is left in the form of bluish-black slender crystals, with an unctuous feel, and staining paper or the skin like plumbago; it admits of being consolidated by pressure, and might, probably, be used in the manufacture of drawing-pencils.

The *tersulphide* (WS_3) may be obtained by dissolving tungstic acid in a solution of sulphide of potassium, and precipitating by the addition of an acid: it is slightly soluble in pure water.

The tersulphide is a strong sulphur acid; with sulphide of potassium it forms an orange-yellow crystallizable compound. These sulpho-salts may be formed by heating the tungstates of the alkalies with an excess of sulphur.

PHOSPHIDES OF TUNGSTEN.—Phosphorus enters into combination with tungsten, when its vapour is passed over the metal in a finely-divided state, and heated to redness in a glass tube; a dull, dark grey powder (W_3P_2), difficult of oxidation, is thus formed. Another compound (W_4P) is formed in beautiful crystalline groups like geodes, by reducing a mixture of 2 atoms of phosphoric and 1 atom of tungstic acid, at a very high temperature, in a crucible lined with charcoal: brilliant six-sided steel-grey prisms, of sp. gr. 5·207, are thus obtained. It is a good conductor of electricity. It is oxidized with difficulty when heated, and is not attacked by acids.

Both the CHLORIDES of this metal (WCl_2) and (WCl_3) are volatile: they are decomposed by water into hydrochloric acid and the corresponding oxide of tungsten. The *terchloride* is formed by passing pure and dry chlorine over heated metallic tungsten; it fuses at 362°, and is of a bronze colour, but by exposure to the air quickly acquires a violet hue, owing to its partial decomposition by the absorption of moisture.

The *oxychloride* (WO_2Cl) may be obtained in yellow volatile crystalline scales, by passing dry chlorine over either the binoxide of

tungsten or tungstic acid when heated to redness. It is sometimes termed chlorotungstic acid. The red volatile compound, formerly supposed to be a terchloride, is, according to Riche, an oxychloride of the form ($WOCl_2$).

Bichloride of tungsten absorbs ammonia, and by a gentle heat, the whole of the chlorine is expelled in the form of sal ammoniac, leaving a black powder consisting of $2\,WN,WH_2N$. When this powder is heated in the air it burns, evolving ammonia and leaving a residue of tungstic acid (Wöhler): it is not soluble in acids.

(698) CHARACTERS OF THE SALTS OF TUNGSTEN.—The compounds of this metal are not poisonous. No salts containing binoxide of tungsten are known.

The *tungstates* in solution are colourless. They are not precipitated either by *sulphuretted hydrogen* or by *hydrosulphate of ammonia.* A *bar of tin,* placed in their acidulated solution in a vessel from which air is excluded, produces a deep violet-coloured liquid, owing to the reduction of the acid to a lower degree of oxidation. Zinc, protochloride of tin, and other reducing agents, in the presence of acids, produce a like result. The addition of any stronger acid to a boiling solution of the tungstates causes the separation of a yellow precipitate of tungstic acid which is soluble in phosphoric and in tartaric acid. They yield *before the blowpipe,* with borax, a colourless transparent glass, which becomes yellow in the reducing flame, and blood-red on cooling. With microcosmic salt (517) they give a beautiful blue in the reducing flame, which becomes yellow or colourless in the oxidating flame; the addition of a little metallic tin to the bead favours the production of the blue colour.

Tungsten is always estimated in the form of tungstic anhydride, 100 grains of which contain 79·32 of the metal.

§ VI. VANADIUM ($V=68{\cdot}46$).

(699) VANADIUM is one of those rare metals at present known only as chemical curiosities: it was discovered in 1830, by Sefström, in a Swedish iron ore from Taberg, which yielded bar iron remarkable for its malleability; but its most abundant ore is the vanadiate of lead, which has been found at Zimapan in Mexico, at Wanlockhead in Scotland, and more recently in Chili; lately Wöhler has found vanadium accompanying some of the ores of uranium and iron. It is best obtained by reducing vanadic acid in a covered porcelain crucible, by means of potassium: the reduc-

tion takes place with vivid incandescence; the potash is dissolved by water, and vanadium is deposited as a brilliant metallic powder. It is readily dissolved by nitric acid and aqua regia, forming a fine blue solution; but it is not acted upon even by boiling sulphuric, hydrochloric, or hydrofluoric acids; when heated with the alkalies in closed vessels, it undergoes no change. By passing a current of dry ammonia over heated chloride of vanadium, a nitride of the metal is obtained in a coherent form with a steel-white lustre; it is brittle and very infusible.

(700) Oxides of Vanadium.—This metal forms three distinct compounds with oxygen, VO; VO_2; and VO_3. The *protoxide* ($VO, = 76.5$) is obtained from vanadic acid, by reducing it, by means of a stream of hydrogen, or by charcoal: it is a black, crystalline, brittle mass, resembling graphite in appearance, and, like it, conducts electricity. It does not combine either with acids or with bases. If heated in air for some time it absorbs oxygen, forming the *binoxide* ($VO_2 = 84.5$), as a black anhydrous powder, which forms salts with acids; they have a blue colour, and when mixed with the alkalies furnish a grey hydrate of the binoxide; in this form it rapidly absorbs oxygen, and becomes first brown and then green. Binoxide of vanadium appears also to possess feebly acid properties, for it combines with bases.

Vanadic anhydride ($VO_3 = 92.5$; *Sp. Gr.* 3.49) is of a brownish-red colour; at a red heat it fuses without further change, and crystallizes on cooling, becoming incandescent from evolution of latent heat in the act of solidification. It is sparingly soluble in water, to which it communicates a yellow tint; the solution is powerfully acid and reddens litmus strongly. It forms both normal and acid salts: the normal salts when first prepared are yellow, but in a few hours they spontaneously become white. The most important of these salts is the *vanadiate ammonia* (H_4NO, VO_3), from which the acid itself is usually obtained. Vanadiate of ammonia is procured by putting pieces of sal ammoniac into a crude solution of vanadiate of potash (such as is prepared by the deflagration of the slag obtained from the iron ore of Taberg, with nitre, after the excess alkali has been neutralized with hydrochloric acid): the vanadiate of ammonia being insoluble in a saturated solution of chloride of ammonium is gradually deposited in small crystalline grains. Cold water dissolves it sparingly, but it is much more soluble in hot water: when heated in the open air the ammonia is expelled, and pure vanadic acid is left. The *acid vanadiate of ammonia* yields crystals of an orange colour. If mixed with tincture of galls, these salts give a deep black liquid,

which preserves its blackness even when much diluted: it forms a very permanent writing ink, since it is not destroyed either by acids, which turn it blue, or by alkalies, or by chlorine.

Vanadic acid appears to combine in different proportions with the inferior oxides of the metal, forming compounds which are either of a green or a purple colour. It also combines with many acids in definite proportions, forming compound acids, such as that with sulphuric acid (VO_3, 3 SO_3): several of these compounds crystallize with facility.

The affinity of vanadium for sulphur is but small. It combines with it in two proportions, VS_2, and VS_3.

A *Bichloride of Vanadium* (VCl_2) may be formed; it is of a blue colour; and a *terchloride* (VCl_3; *Sp. Gr. of vapour,* 6·41, *of liquid,* 1·764; *Boiling pt.* 260°) which is a yellow, fuming, volatile liquid, is obtained by heating a mixture of vanadic acid and charcoal in a current of chlorine. Bromides, iodides, fluorides, and cyanides of vanadium have also been formed.

(701) CHARACTERS OF THE COMPOUNDS OF VANADIUM.—1. The salts of the *binoxide of vanadium* yield blue solutions, which give a black colour with *tincture of galls*, and a grey precipitate with the *alkalies*, becoming red by exposure to the air. *Ferrocyanide of potassium* gives a yellow precipitate, which becomes green when exposed to the air. The *sulphides* of the alkaline metals give a brownish-black precipitate, readily soluble in excess, and forming a magnificent purple liquid.

2.—The *vanadiates*, when treated with sulphuretted hydrogen, or when boiled with sulphuric acid and either alcohol or sugar, give a beautiful blue solution, a reaction that distinguishes them from the chromates, which under these circumstances furnish a green liquid. *Before the blowpipe* with borax in the reducing flame, compounds containing vanadium give a green glass, which becomes yellow in the oxidating flame.

§ VII. ARSENIC (As=75). *Sp. Gr. of Vapour,* 10·69; *of Solid, from* 5·70 to 5·959. *Comb. Vol.* 1.

(702) ARSENIC, in various states of combination, was known to mankind before the Christian era. This element presents many analogies with phosphorus, and with nitrogen: it is considered by several French writers to belong to the non-metallic elements. It, however, conducts electricity with facility, and possesses a high metallic lustre. Arsenic generally presents itself in the form of an alloy with some other metal, especially with iron, or with cobalt,

nickel, copper, or tin. It is found occasionally in the native state, and it sometimes occurs united with oxygen combined as arsenic acid with other oxides, constituting arseniates, such as those of iron, copper, and lead. More rarely it occurs united with sulphur, either as the red bisulphide (realgar), or as orpiment, the yellow tersulphide.

The greater part of the arsenic of commerce is prepared from mispickel ($FeAs,FeS_2$), an arsenical sulphide of iron, furnished abundantly by the Silesian mines; and from the arsenides of nickel and cobalt, which yield arsenious acid as a secondary product in the ordinary process of working these ores. The separation of the arsenic is effected by roasting the mineral in a manner similar to that employed for driving off sulphur; but the arsenious acid which is produced, being less volatile, more valuable, and more deleterious, is condensed in large chambers, through which the flues from the furnaces pass. The emptying of these chambers, which is performed about once in six weeks, is an operation attended with danger to the workmen, from the poisonous and irritating nature of the finely-powdered arsenious acid. In order in some degree to protect the men whilst thus engaged, they are cased in leather, with glazed apertures for the eyes, and are made to cover their mouths and nostrils with damp cloths, which arrest most of the acrid particles. Much of the acid obtained from these chambers is in the form of a fine powder; it is still very impure, and it is therefore again sublimed in iron pots, the upper part of which is kept moderately cool; here it is condensed into a transparent, half-fused, vitreous mass. The lower portions only of this sublimate are pure, and these are sold as white arsenic; the upper are either resublimed, or are employed for the pupose of furnishing metallic arsenic. In order to obtain the metal, the sublimed acid is powdered, mixed with charcoal, or with twice its weight of black flux, and heated in an earthen crucible, upon the top of which a second inverted crucible is luted, and screened from the fire by means of a perforated iron plate. The reduced metal is condensed in the upper crucible.

Properties.—Metallic arsenic, or *arsenicum*, as it might conveniently be termed, has a brilliant, dark steel-grey lustre; it is very brittle, and is easily reduced to powder. When heated to 356° in closed vessels, it begins to volatilize without fusing, and crystallizes indistinctly, as it is condensed, in rhombohedra, which are isomorphous with those of antimony. Its vapour is colourless, and possesses a powerful, oppressive, alliaceous odour; its combining volume is the same as that of oxygen and phosphorus. The metal may be exposed to a dry air without undergoing change:

when exposed in a moist state to the air it is slowly oxidized, and a substance known as *fly-powder* is formed; it is probably a mixture of arsenious acid and metallic arsenic, though it is regarded by some chemists as a suboxide. If the metal be heated in open vessels it absorbs oxygen, burns with a peculiar bluish flame, and is converted into arsenious acid, which is condensed as a white, mealy powder, upon cool bodies in the neighbourhood. When thrown in fine powder into chlorine gas it takes fire spontaneously, and is converted into chloride of arsenic. Bromine, iodine, and sulphur also combine readily with arsenicum when aided by a gentle heat. Nitric acid easily oxidizes the metal, and converts it into arsenic acid: if deflagrated with nitre, it is converted into arseniate of potash. Hydrochloric acid exerts but little action on the metal, but if this acid be mixed with nitric acid, or with chlorate of potash, the metal is rapidly converted into arsenic acid.

A minute quantity of arsenic is added to lead to facilitate its assuming the globular form in the manufacture of shot. In the form of arsenious acid it is extensively used in the preparation of green and yellow pigments; it is likewise employed to prevent smut in grain; and is used in the manufacture of flint glass as an oxidizing agent, for converting the protoxide of iron into peroxide, in order to get rid of the green tinge which protoxide of iron communicates to the vitreous mass. Its employment as a poison for vermin has often been made a pretext for procuring it for criminal purposes.

Oxides of Arsenic.—These are two in number; both have acid properties, no salifiable oxide being known; they have the following composition:—

		Oxygen. Arsenic.
Arsenious anhydride,	AsO_3	$24{\cdot}25 + 75{\cdot}75$
Arsenic anhydride,	AsO_5	$34{\cdot}78 + 65{\cdot}22$

(703) *Arsenious Acid* or *Arsenious Anhydride* ($AsO_3 = 99$); *Sp. Gr. of vapour*, $13{\cdot}85$; *Comb. Vol.* 1.—This compound is the *white arsenic* of the shops. It is prepared upon the large scale during the roasting of arsenical ores in the manner already described. It exists in two modifications, a vitreous and a crystalline form. When purified by resublimation and freshly obtained, it is in semi-transparent, vitreous, lamellated masses; but by exposure to the air, it gradually becomes opaque, and of a yellowish-white colour. This change advances slowly, from the exterior towards the interior, so that the mass is often opaque at the surface whilst it remains transparent in the centre. Both varieties of arsenious acid are freely soluble in hot hydrochloric acid; when this solution is boiled, a portion of the arsenic is volatilized in the form of ter-

chloride; as the liquid cools the excess crystallizes in transparent anhydrous octohedra, consisting of uncombined arsenious acid; but when the transparent variety has been employed, the formation of each crystal is marked by the emission of a flash of light which is perceptible in a darkened room. The opaque variety exhibits no such phenomenon in crystallizing from its solution. A hot solution of ammonia also dissolves arsenious acid freely, and deposits it in anhydrous octohedra of the uncombined acid on cooling, mixed with prismatic crystals of dibasic arsenite of ammonia (Bloxam). Guibourt found the opaque variety to have a specific gravity of 3·699; it is less dense than the transparent form, the specific gravity of which he states to be 3·7385. The two varieties also differ in their solubility: according to Bussy (*Comptes Rendus*, Mai, 1847), water dissolves much less of the opaque than of the transparent acid. A cold saturated solution of the vitreous variety gradually deposits its excess of acid in the opaque form, and retains between 2 and 3 per cent. in solution; the liquid reddens litmus. Mere grinding to a fine powder converts the transparent into the opaque variety, and reduces its solubility. Heat, however, gradually reconverts the opaque into the vitreous modification, so that long-continued boiling renders the opaque as soluble as the vitreous form. It is therefore difficult to state the precise degree of solubility of either form of the acid, because the two varieties are liable to be formed in varying proportion in the course of an experiment. The largest proportion which water will dissolve at the boiling point is between 11 and 12 per cent. Both nitric acid and aqua regia dissolve arsenious acid, and convert it into arsenic acid.

Arsenious acid, when heated to 380°, softens and is sublimed without fusing, being condensed in transparent octohedra upon warm surfaces, but it occasionally forms long prismatic needles, isomorphous with those of oxide of antimony. Its vapour is without odour; it is colourless, and contains 1 volume of vapour of arsenic and 3 volumes of oxygen, condensed into 1 volume.

Arsenites.—Arsenious acid is soluble in solutions of the alkalies and of their carbonates: with potash and soda it forms soluble compounds which do not crystallize. Arsenite *of potash* has been used medicinally for many years under the name of *Fowler's Solution.* The arsenites of the earths (particularly arsenite of lime) are nearly insoluble in water, but are readily dissolved by acids. Arsenite *of copper* ($2\,CuO,AsO_3$) is, in a commercial point of view, the most important of these salts; it is of a delicate and beautiful green colour, constituting the pigment sold under the name of

Scheele's green. It is prepared by dissolving 1 part of arsenious acid and 3 parts of carbonate of potash in 14 of water, and adding the liquid to a boiling solution of 3 parts of sulphate of copper in 40 of water: the shade of green may be varied by altering the proportion of arsenious acid. This compound is a dangerous poison. It is soluble in acids and in ammonia. When heated it is partially decomposed, and arsenious acid sublimes. The *Schweinfurt green,* which is also used largely as a pigment, is a double salt of arsenite and acetate of copper [$3\,(CuO,AsO_3) + CuO,C_4H_3O_3$], made by mixing equal parts of arsenious acid and acetate of copper, in solution at a boiling temperature, adding an equal bulk of cold water, and allowing the mixture to stand for some days. Arsenite *of silver* ($3\,AgO,AsO_3$) is of a canary-yellow colour; it is obtained by the addition of a solution of nitrate of silver to one of arsenite of potash. If a slip of bright copper foil be introduced into a solution of arsenious acid in hydrochloric acid, a grey film of reduced arsenic is deposited on the copper; if zinc be substituted for copper, arseniuretted hydrogen is evolved (708, 709). Arsenious acid in solution may readily be converted into arsenic acid by acidulating the liquid with hydrochloric acid, warming it, and gradually adding chlorate of potash in small quantities. Arsenious acid is indeed a powerful reducing agent; its solution in hydrochloric acid reduces terchloride of gold; it bleaches permanganate of potash, and reduces bichromate of potash to a sesquisalt of chromium.

If a solution of arsenious acid in carbonate of soda be mixed with a little starch, and a solution of iodine or of chlorine be added, the arsenious is converted into arsenic acid; this reaction forms the basis of a volumetric process for the determination of iodine and chlorine in solution.

If a minute fragment of arsenious acid be heated with a similar portion of acetate of soda in a small test-tube, the characteristic and peculiarly offensive odour of kakodyl is perceived.

(704) *Arsenic Acid* ($AsO_5 = 115$) is obtained by treating arsenious acid with nitric acid in excess, and then boiling down to dryness in a platinum vessel. A white, anhydrous, somewhat deliquescent mass remains: by slow evaporation of its solution arsenic acid may be obtained in hydrated crystals ($3\,HO,AsO_5 + Aq$), which are very deliquescent; they fuse at 212°, and lose their water of crystallization. No attempts to procure the dibasic and monobasic forms of arsenic acid have hitherto been successful; but it has been procured in the form of definite hydrates, $3\,HO,AsO_5$; $2\,HO,AsO_5$; and HO,AsO_5; which, when redissolved in water, all

present the properties of the tribasic form. The first is obtained by evaporating the ordinary aqueous solution at 212°; if the temperature be raised to 300° hard prisms of the dihydrate are procured; and at a temperature of 400° these are converted into pearly scales of the monohydrate: at a temperature approaching to redness the mass becomes anhydrous, and if heated still more strongly it fuses, and then becomes decomposed into arsenious acid and oxygen. If a current of sulphurous acid be transmitted through its solution, the arsenic is slowly reduced to the state of arsenious acid, whilst sulphuric acid is formed, $AsO_5 + 2\ SO_2$ becoming $AsO_3 + 2\ SO_3$. Arsenic acid has recently been employed in calico printing to some extent as a substitute for tartaric and phosphoric acids, but its employment is dangerous if the waste products are allowed to run into the streams.

Arseniates.—The arsenic is a powerful acid, expelling the volatile acids from their combinations, and decomposing the carbonates with effervescence. It forms a series of soluble crystallizable salts with the alkalies, which present considerable interest, as they are isomorphous with the tribasic phosphates. Salts of this acid may be obtained with 3 atoms of fixed base, as well as with 1 and with 2 atoms of basic water. By adding soda in excess to arsenic acid, an efflorescent salt ($3\ NaO,AsO_5 + 24\ Aq$) may be obtained on evaporation, crystallized in prismatic needles. If to a hot solution of arsenic acid carbonate of soda be added till effervescence ceases, the salt which is obtained on evaporation ($HO, 2\ NaO,AsO_5 + 24\ Aq$) corresponds in form and composition to the rhombic phosphate of soda, though more usually it crystallizes with 14 Aq; and by adding to a solution of this compound a quantity of arsenic acid, equal to that which it contains, a deliquescent salt ($2\ HO,NaO,AsO_5 + 2\ Aq$) is procured, which crystallizes with difficulty. The corresponding potash-salt crystallizes in bold, brilliant octohedral crystals ($2\ HO,KO,AsO_5$): it is readily prepared by deflagrating equal parts of arsenious acid and nitre, then dissolving the residue in water, and allowing it to crystallize. All these salts may be rendered anhydrous by heat, but when redissolved, they recover their basic water. An arseniate of magnesia and ammonia ($H_4NO,2MgO,AsO_5 + 12\ Aq$) may be procured in the form of prismatic crystals isomorphous with the corresponding phosphate by mixing a solution of sulphate of magnesia containing an excess of ammonia, with a neutral or ammoniacal solution of an arseniate of one of the alkalies: it is sometimes used as a precipitant for arsenic acid; it is very sparingly soluble in weak ammoniacal solutions; when dried at 212° it loses 11 Aq, and the

dried salt contains 60·52 parts of arsenic acid. A brick-red triarseniate of silver ($3\ AgO,AsO_5$) is precipitated when any arseniate in solution is mixed with a solution of nitrate of silver: it is readily soluble in excess either of nitric acid or of ammonia, and is characteristic as a test of arsenic acid. The arseniate of copper ($2\ CuO,HO,AsO_5$) is of a pale greenish-blue colour; those of lime and lead are white; whilst the salts of peroxide of iron and of uranium give yellowish-white arseniates, readily soluble in excess of diluted nitric acid.

(705) SULPHIDES OF ARSENIC.—Arsenicum and sulphur may be melted together in all proportions; but they form several well-defined compounds: of these, the most important are the bisulphide, or realgar, AsS_2; the tersulphide, or orpiment, AsS_3; and the pentasulphide or sulpharsenic acid, AsS_5.

Bisulphide of Arsenic, or *Realgar* ($AsS_2=107$); *Sp. Gr.* 3·356.—This substance is occasionally found native in ruby-red prismatic crystals: it may be prepared artificially, by heating together 7 parts of arsenicum and 4 of sulphur, or 198 parts of arsenious acid with 112 of sulphur; in the latter case 3 equivalents of sulphurous acid are expelled, and 2 of realgar are formed: $2\ AsO_3 + 7\ S = 2\ AsS_2 + 3\ SO_2$. When heated in closed vessels, realgar melts, and afterwards is sublimed without decomposition. The sublimed mass is hard, brittle, transparent, and of a beautiful red colour. Realgar is insoluble in water: it is readily attacked by nitric acid and by aqua regia, but not by hydrochloric acid; sulphide of potassium dissolves it and forms a double sulphide. Caustic potash decomposes it, leaving a brown subsulphide of arsenic (As_6S) undissolved. Realgar is one of the ingredients of *white Indian fire*, which is often used as a signal light: it is composed of a mixture of 7 parts of sulphur, 2 of realgar, and 24 of nitre.

Tersulphide of Arsenic, Sulpharsenious Acid, or *Orpiment* ($AsS_3=123$); *Sp. Gr.* 3·48.—Orpiment is occasionally found native in crystals which have the same form as those of realgar—viz., the oblique rhombic prism: these crystals are flexible; they have a yellow colour and a brilliant lustre. It may be prepared artificially by transmitting a current of sulphuretted hydrogen through a solution of arsenious acid, or of any of the arsenites, in hydrochloric acid; it then falls as a brilliant yellow amorphous powder. If the solution be very dilute, part of the sulphide is retained in solution, forming a yellow liquid; by exposure to the air the excess of sulphuretted hydrogen escapes, and the tersulphide is gradually and completely deposited.

Tersulphide of arsenic is insoluble in water and in dilute acids,

but it is decomposed by nitric acid and by aqua regia. It fuses easily, and when heated in air burns with a pale blue flame. In closed vessels it may be sublimed without undergoing decomposition. Ammonia and the fixed alkalies dissolve it, and form colourless solutions containing an alkaline arsenite and sulpharsenite. The ammoniacal solution is sometimes used for dyeing yellow, since by exposure to air the ammonia evaporates, leaving the yellow sulphide firmly adherent to the fibre. Orpiment is also soluble in a solution of sesquicarbonate of ammonia. Tersulphide of arsenic is a feeble sulphur acid, so that hydrosulphate of ammonia and the sulphides of the alkaline metals in solution dissolve it easily, and form double sulphides which are decomposed on the addition of an acid. Orpiment is the colouring ingredient in the pigment called *King's yellow*, which is a mixture of arsenious acid with this sulphide.

Pentasulphide of Arsenic ($AsS_5 = 155$), or *Sulpharsenic Acid*, as it is sometimes called, corresponds in composition to arsenic acid. It is prepared by transmitting a stream of sulphuretted hydrogen through a solution of arsenic acid; a yellow precipitate, resembling orpiment in appearance, is very gradually separated. Upon the application of heat, the pentasulphide fuses into a dark liquid, and forms a reddish-yellow glassy substance as it cools; it may be sublimed in closed vessels. It is soluble in the alkalies, decomposes the carbonates with effervescence if boiled with their solutions, and forms crystallizable compounds with the sulphides of the metals of the alkalies and alkaline earths. The sulphur-salt of potash ($2\,KS,AsS_5$) may be made by transmitting sulphuretted hydrogen through the solution of the diarseniate of potash. When this sulphur-salt of arsenic is mixed with alcohol, it undergoes decomposition, and by evaporating the alcoholic solution, after separating the insoluble portion by filtration, a still higher sulphide (AsS_{18}) was obtained by Berzelius, in brilliant yellow crystalline scales.

(706) COMPOUNDS OF ARSENIC WITH HYDROGEN.—Arsenic forms two combinations with hydrogen; one of these is solid at ordinary temperatures, and of a chestnut-brown colour; it is obtained by employing a plate of arsenicum as the platinode during the voltaic decomposition of acidulated water; its composition has not been accurately determined. The other is a gaseous body (H_3As) of considerable importance; it corresponds in composition to the gaseous phosphuretted hydrogen.

Terhydride of Arsenic; Arseniuretted Hydrogen ($H_3As = 78$); *Sp. Gr.* 2·695, *Comb. vol.* 4.—This remarkable gaseous compound

is an exceedingly poisonous body; it is colourless, and has a fœtid alliaceous odour; it is sparingly soluble in water, and possesses neither acid nor alkaline qualities. It consists of 1 volume of arsenical vapour and 6 volumes of hydrogen condensed into 4 volumes. By a temperature of $-40°$ it is reducible to a limpid colourless liquid, which remains liquid at $-166°$ F. Arseniuretted hydrogen is inflammable, and burns with a bluish-white flame, which deposits arsenicum upon cold bodies introduced within it, and arsenious acid upon those held above. It is also decomposed when caused to pass through tubes heated to a temperature a little short of redness, metallic arsenic being deposited as a steel-grey crust, whilst hydrogen gas escapes; if a current of dry sulphuretted hydrogen be transmitted over the heated crust a yellow sublimate of sulphide of arsenic is formed which is not acted on by a current of hydrochloric acid gas. These reactions distinguish the arsenical from an antimonial crust, which by similar treatment gives a dark orange-coloured sulphide decomposed by a current of dry hydrochloric acid gas. Chlorine decomposes arseniuretted hydrogen with flame, forming hydrochloric acid, and causing the deposition of a solid brown hydride of arsenic. This gas is entirely absorbed by a solution of sulphate of copper, sulphuric acid being liberated, whilst arsenide of copper is precipitated. Nitrate of silver is also decomposed by arseniuretted hydrogen. Solution of corrosive sublimate likewise dissolves it completely, a compound of calomel and arsenide of mercury being formed. It is also largely absorbed by oil of turpentine, with which it forms a crystalline compound.

Pure arseniuretted hydrogen may be prepared by decomposing with sulphuric acid diluted with three parts of water, an arsenide of zinc, obtained by heating equal weights of powdered arsenicum and granulated zinc in an earthen retort; the fused mass is removed by breaking the retort, and is subsequently powdered. The greatest care is required not to inhale any portion of this deadly gas.

(707) TERCHLORIDE OF ARSENIC ($AsCl_3 = 181{\cdot}5$; *Sp. Gr. of vapour,* 6·3; *of liquid at* 32°, 2·205; *Boiling pt.* 270°.)—Only one compound of arsenic with chlorine is known. It is produced either by the combustion of the metal in chlorine, or still better by distilling a mixture of 1 part of arsenicum and 6 parts of corrosive sublimate; it condenses as a heavy, colourless, oily-looking liquid, which remains liquid at $-20°$; it fumes when exposed to the air, and is immediately decomposed by water into arsenious and hydrochloric acids.

Teriodide of Arsenic ($AsI_3=456$) may be prepared by subliming a mixture of 3 parts of iodine and 1 part of the metal in a flask; it forms brick-red brilliant flakes. It may also be obtained by digesting 3 parts of powdered arsenic and 10 of iodine in 100 of water; the clear liquid yields red hydrated crystals on evaporation, which become anhydrous when heated to their fusing point: it is soluble in alcohol.

A *terbromide* may be formed by analogous means; it is a crystalline solid at all temperatures below 68°.

The *terfluoride* may be prepared by distilling 5 parts of fluor-spar, mixed with 4 of arsenious acid and 10 of concentrated sulphuric acid. It is a fuming colourless liquid, which rapidly corrodes glass, and is decomposed by water.

(708) Characters of the Compounds of Arsenic.—Arsenicum forms, with most of the metals, alloys which are generally brittle and easily fusible. The compounds of this metal are all highly poisonous:* the substance which has the best claim to be considered as an antidote to it is the freshly-precipitated hydrated oxide of iron, which should be suspended in water, and given freely, as early as possible after the exhibition of the poison. It is only applicable when arsenic or arsenious acids have been taken, as it forms an insoluble arseniate of iron; the arsenious acid being partially oxidized by the excess of hydrated peroxide, which is thereby reduced to the form of protoxide of iron. Calcined magnesia may be used if the oxide of iron be not at hand. In cases of arsenical poisoning, putrefaction of the body after death is retarded in a remarkable degree; indeed, in several instances where the body has been disinterred several months after death, it has been found to have been sufficiently preserved from decay to allow many of the principal viscera to be distinguished. In these cases it has not unfrequently happened that yellow patches of sulphide of arsenic have been observed in various parts of the alimentary canal, although it has been ascertained that the poison had been swallowed in the form of arsenious acid. These patches of orpiment are occasioned by the disengagement of sulphuretted hydrogen from the decomposition of the tissues, by which the arsenious acid becomes partially converted into the tersulphide of the metal.

Arsenic can be identified in quantities so minute as to be inappreciable by the balance. In minerals which contain it, its

* For a singular statement respecting the arsenic eaters of Styria, the reader is referred to a paper by Mr. Heisch, in the *Pharmaceutical Journal* for May, 1860, p. 556.

presence is revealed by the peculiar garlic odour which it emits when a fragment is heated in the reducing flame with carbonate of soda on charcoal, *before the blowpipe*. When in solution, the compounds of arsenic may be detected by transmitting through the solution, acidulated with acetic acid, a stream of *sulphuretted hydrogen* for six hours; a yellow precipitate is thus produced, which must be further examined as follows: the liquid must be exposed to a temperature of about 100° F., in a shallow vessel for six hours, to allow the excess of gas to escape, and the precipitate to subside completely; the clear liquid must be decanted, and the precipitate collected on a small filter. A few drops of ammonia will dissolve it, and on evaporating this solution in a watch-glass by means of a water-bath, the tersulphide of arsenic will be left. This substance is then subjected to the process of *reduction*, by mixing it with three times its bulk of black flux,* or with a mixture of 1 part of cyanide of potassium and 3 parts of carbonate of soda, previously well dried, and introducing it into a glass tube of the diameter of a common quill, care being taken not to soil the sides of the tube. The mixture is heated strongly by the blowpipe, and the arsenic is condensed as a brilliant mirror-like ring of steel-grey lustre in the upper part of the tube. The reaction which occurs when carbonate of potash is used, is explained by the following equation:—

$$AsS_3 + 3\,(KO,CO_2) + 3\,C = As + 3\,KS + 6\,CO.$$

Sulphide of cadmium gives a yellow precipitate with sulphuretted hydrogen, but it is insoluble in ammonia: persalts of tin also give a yellow precipitate with sulphuretted hydrogen, but no metallic crust when they are submitted to the process of reduction.

In addition to the preceding tests, arsenious acid may be readily detected in a *neutral* solution by the production of a yellow precipitate with the *ammonia-nitrate of silver*. This reagent is prepared by adding ammonia to a solution of nitrate of silver in very slight excess, so as nearly, but not entirely, to redissolve the precipitate of oxide of silver which is at first formed: the clear liquid is decanted for use. The yellow precipitate is an arsenite of silver, which is freely soluble both in ammonia and in nitric acid. As, however, the tribasic phosphates give a yellow precipitate with ammonia-nitrate of silver, and this precipitate also is soluble both in nitric acid and ammonia, a second test should be tried—viz., the *ammonia-sulphate of copper*, which is prepared from a solution

* A mixture of carbonate of potash and charcoal obtained by deflagrating equal weights of cream of tartar and nitre in a red-hot earthen crucible.

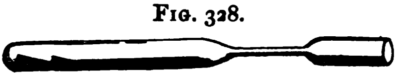
of sulphate of copper, by the addition of ammonia, with the same precautions as those prescribed for the preparation of the silver test. In neutral solutions containing arsenious acid, this copper test occasions a green precipitate consisting of arsenite of copper: it is soluble both in ammonia and in acids. The arsenites of silver and of copper are formed immediately that the tests are added; the sulphide of arsenic does not appear at first if the quantity of arsenious acid be small, as the compounds of arsenic are decomposed by hydrosulphuric acid more slowly than those of any other metal which is precipitable by this reagent.

(709) *Search for Arsenic in Organic Mixtures.*—In the greater number of cases, however, where the search for arsenic becomes important, it is mixed with articles of diet, with the contents of the stomach, or with other matters of organic origin, which render preliminary measures needful in order to get rid of them. If the substance be in the liquid form, any sediment which it may contain must be examined for solid particles of undissolved arsenious acid, which are frequently found, and to which the preceding tests are readily applied. If any solid particles of arsenious acid be found, their reduction is easily effected by drawing off a tube to the thickness of a crowquill, sealing one end, dropping in the suspected fragment, adding a minute quantity of dried carbonate of soda, and then a few small fragments of charcoal; upon ignition, the metal is sublimed, and may be recognised by the steel-grey ring which it forms in the cool portion of the tube.

If no solid particles of the acid be visible, the liquid is boiled and filtered, and divided into three portions, one of which is set aside in case of accident.

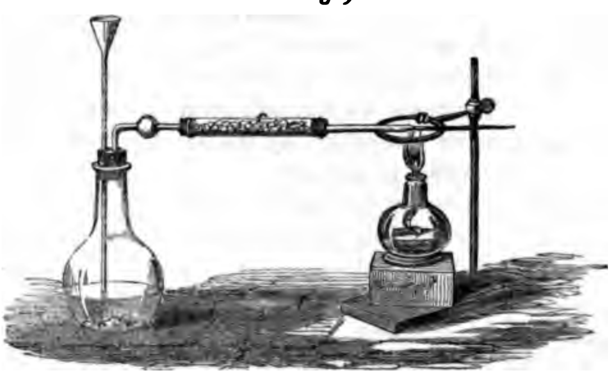
A second portion is submitted to *Reinsch's test*; it is for this purpose acidulated with about $\frac{1}{10}$th of its bulk of hydrochloric acid, and boiled with bright slips of pure electrotype copper foil for half an hour. If any arsenical compound be present, the metal will be reduced upon the surface of the copper foil. The copper is then withdrawn from the liquid, washed, dried at 212°, and introduced into a narrow glass tube (of about the diameter of a quill), which is then drawn out to a capillary neck, taking care not to heat the copper foil in this operation. The tube is shown in fig. 328. The foil, and the portion of the tube which contains it, are then heated nearly to redness; the arsenic combines with oxygen derived from the air in the tube, and is condensed in beautiful transparent octohedra of arsenious acid on the contracted cool

FIG. 328.



part of the tube. The same experiment must be first tried with the copper and hydrochloric acid employed alone, in order to ascertain their purity, before employing them as tests. The presence of nitrates or of chlorates interferes with the application of Reinsch's test, as the copper foil becomes dissolved when boiled with the acidulated solution under these circumstances. If, however, the liquid be acidulated with an excess of hydrochloric acid, and be evaporated by a gentle heat on a water-bath, the residue may be subjected to Reinsch's process as usual. A slip of metallic copper occasions precipitates in many metallic solutions when acidulated with hydrochloric acid and boiled with them; such, for example, as antimony, bismuth, tin, silver, mercury, lead, and cadmium: cadmium is not precipitable from a strongly acid solution. Of these precipitates mercury is the only one which, like arsenic, is volatilized by heat, but the sublimate, when viewed with the microscope, is seen to consist of globules, and is thus easily distinguished from arsenic. Moreover the arsenical crust by resublimation is converted into arsenious acid, whilst no such change takes place with mercury.

FIG. 329.



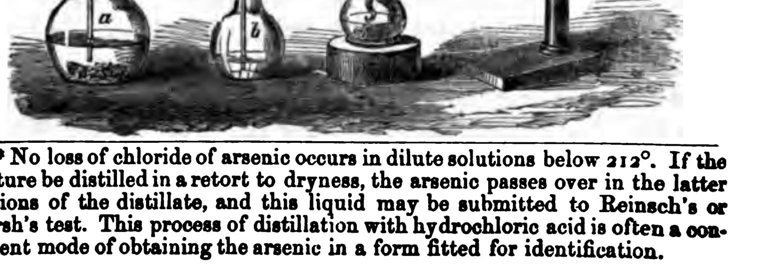
The third portion of the liquid is subjected to *Marsh's test:* the application of this test depends upon the formation of arseniuretted hydrogen, and the subsequent deposition of arsenic from it by suitable application of heat:—A wide-mouthed flask, fig. 329, of about 6 oz. capacity, is charged with a little pure granulated zinc; through the cork a tube funnel is passed to within an inch of the bottom; a bulb tube, bent to a right angle, passes just through the cork, the outer horizontal tube *c*, being loosely filled with chloride of calcium to arrest any particles of fluid which might be carried up by the effervescence; it is prolonged by fitting into it with a cork, a piece of German tube, *a*, free from lead and drawn out to a capillary termination. Some distilled water is next intro-

duced by the funnel, and a little pure sulphuric acid added to cause a steady evolution of hydrogen. When all the atmospheric air is expelled, the flame of a spirit-lamp is placed under the point where the capillary contraction commences: if after ten minutes, the temperature of the glass being at a red heat, no indications of any metallic deposit show themselves, the materials used are sufficiently pure. Whilst the heat is still maintained, the suspected liquid is to be poured through the funnel into the bottle; if arsenic be present, immediate voltaic decomposition ensues, part of the arsenic combines with the nascent hydrogen; arseniuretted hydrogen is formed, and the gas is decomposed as it passes through the heated tube, the metal being deposited in the form of a steel-grey ring just beyond the spot where the heat is applied. If, instead of heating the capillary tube, the gas be kindled as it escapes, it will be found to burn with the peculiar flame of arsenic if the quantity be at all considerable, and if a piece of cold white porcelain, such as a crucible lid, be introduced into the burning jet, the more combustible hydrogen is burned, and brown or grey mirror-like spots of reduced arsenic may be obtained upon the cold plate. Tartar emetic, if present, would, however, produce antimoniuretted hydrogen, which, by its decomposition, would give rise to appearances on the tube and on the porcelain resembling those of arsenic. The antimonial spots immediately disappear when a drop of hydrosulphate of ammonia, in which a little sulphur is dissolved, is added, and the solution, by its spontaneous evaporation, leaves the orange hydrated tersulphide of antimony; but the arsenical crusts are scarcely acted on by the hydrosulphate (Dr. Guy): a drop of a dilute solution of chloride of lime, on the other hand, immediately removes the arsenical spot, but is without action on that produced by antimony. The chief practical difficulty in the use of Marsh's test, arises from the inconvenient way in which liquids containing organic matter frequently froth up during the operation. The best method of preventing this consists in first heating the suspected liquid with about a tenth of its bulk of hydrochloric acid, and adding a small quantity of chlorate of potash: the organic matter is thus destroyed, and after the liquid has become cool, it may be safely added to the zinc and sulphuric acid in the apparatus. Marsh's test is one of extraordinary delicacy, and the results are easily and quickly attained. The process by sulphuretted hydrogen and subsequent reduction is also extremely delicate, and open to no objection except the length of time required. Reinsch's test is easy of application, and is likewise extremely delicate. The arsenical crusts deposited in

the glass tube, are readily sublimed by a gentle heat, and may be converted into arsenious acid, which forms brilliant minute octohedral crystals, and these again may be subjected to the test of the ammonia-nitrate of silver.

Although it may not be possible to detect arsenic in the fluids submitted to examination, it not unfrequently happens that the coats of the stomach, and sometimes the liver, will yet contain the poison in sufficient quantity to render its identification practicable. The best mode of proceeding in this case consists in cutting up the organ into shreds, heating it on a water-bath with a fourth of its weight of hydrochloric acid, the mixture being diluted with water till it becomes of the consistency of a thin paste. Small portions of chlorate of potash are added from time to time until a homogeneous yellow liquid is obtained; when cold it is filtered through linen, the residue well washed, and the clear liquid is concentrated by evaporation by a heat not exceeding that of the water-bath* (Fresenius and Von Babo, *Liebig's Ann.*, xlix. 287). It is then fit for trial in Marsh's apparatus. Fresenius and Von Babo prefer to reduce the arsenic acid in the liquid to arsenious acid by means of a current of sulphurous acid gas. They then heat gently to expel the excess of sulphurous acid, precipitate the arsenic by sulphuretted hydrogen, collect the precipitate on a small filter, wash, dissolve out the sulphide of arsenic with ammonia, evaporate the solution on a watch-glass, and reduce the sulphide by mixing it with about 12 times its weight of a mixture of 3 parts of dried carbonate of soda and 1 of cyanide of potassium, and heating it in a very slow current of dried carbonic acid gas, as shown in fig. 330, in which *a* repre-

FIG. 330.



* No loss of chloride of arsenic occurs in dilute solutions below 212°. If the mixture be distilled in a retort to dryness, the arsenic passes over in the latter portions of the distillate, and this liquid may be submitted to Reinsch's or Marsh's test. This process of distillation with hydrochloric acid is often a convenient mode of obtaining the arsenic in a form fitted for identification.

sents a flask containing fragments of marble from which the carbonic acid is disengaged by the addition of hydrochloric acid: *b* contains oil of vitriol in order to dry the issuing gas; the arsenical mixture is placed in the bend of the tube *c*, and the metallic crust sublimed into the contracted part of the tube at *d*. This process is complicated, and not superior to Reinsch's if the latter be conducted with due care. A very delicate mode of detecting the presence of arsenic is afforded by the action of the voltaic current, which may be applied without difficulty by adopting the precautions recommended by Bloxam (*Q. J. Chem. Soc.*, xiii. 12). The galvanic process has the advantage of being applicable to the detection of various other metallic poisons if arsenic be absent, as nothing is introduced which interferes with their identification subsequently by appropriate tests.

(710) *Estimation of Arsenic.*—It is not easy to ascertain accurately, by analysis, the quantity of arsenic present in a compound; but the following is the plan generally adopted:—The metal is precipitated in the form of a sulphide; the precipitate collected on a weighed filter, dried at 212°, and weighed: a given weight of the sulphide is then oxidized by means of nitric acid (sp. gr. 1·51); and when it is completely dissolved, the sulphur is precipitated as sulphate of baryta. From the weight of this precipitate the quantity of sulphur is calculated, and deducted from the total amount of sulphide of arsenic; the difference gives the amount of the metal. The sulphide is apt to contain a variable quantity of free sulphur, and hence this method becomes necessary. Before it can be adopted, the absence of all other metals in the sulphide must, of course, be ascertained. The arsenic acid in the solution may further be precipitated as arseniate of magnesia and ammonia, by neutralizing with ammonia, and adding a solution of sulphate of magnesia containing chloride of ammonium and ammonia in excess: 100 parts of this precipitate dried at 212° (H_4NO, $2\,MgO,AsO_5 + Aq$) represent 39·47 of metallic arsenic.

(711) *Separation of Arsenic from other Metals.*—By means of sulphuretted hydrogen and the subsequent solution of the sulphide in hydrosulphate of ammonia, arsenic is easily separated from all the foregoing metals, with the exception of those which form soluble compounds with the sulphides of the alkaline metals. A solution of sesquicarbonate of ammonia (free from uncombined ammonia), when digested on the mixed hydrated sulphides of arsenic and antimony, dissolves the arsenical sulphide only, and leaves it on evaporation. The two metals also may be separated by Bunsen's method with bisulphite of potash (722).

§ VIII. ANTIMONY (Sb=122). *Sp. Gr.* 6·715.

(712) ANTIMONY was well known to the alchemists. It is a brilliant bluish-white metal, of a flaky, crystalline texture, and so brittle that it may readily be reduced to powder. It fuses at about 840°, and by slow cooling may be obtained in rhombohedral crystals, which, according to Mitscherlich, are isomorphous with those of arsenic. The commercial cakes of the metal exhibit upon their upper surface a beautiful penniform crystalline structure. At a bright red heat it is volatilized slowly; the operation is facilitated by transmitting a current of hydrogen over it. Antimony is inferior to most of the metals as a conductor of heat and of electricity. When exposed to either a moist or a dry air, at ordinary temperatures, it undergoes no change, but if heated it burns brilliantly, emitting copious white fumes which consist chiefly of teroxide of antimony. Powdered antimony takes fire spontaneously when thrown into chlorine gas; bromine and iodine also enter into combination with the metal with great evolution of heat when they are brought into contact with it at ordinary temperatures. It is also oxidized by nitric acid and by boiling sulphuric acid. Aqua regia dissolves it readily. When finely powdered, it is dissolved by strong hydrochloric acid by the aid of heat, with evolution of hydrogen. Metallic antimony, when in fine powder, is readily dissolved by digestion with a solution of one of the higher sulphides of potassium, whilst the lead, iron, copper, bismuth, or silver which it may contain is left undissolved. Small quantities of arsenic and of tin, if present, enter into solution with the antimony.

Alloys.—This metal is not used alone in the arts, but it enters into the composition of several valuable alloys. *Type metal* is one of these: it is composed of 3 or 4 parts of lead, and 1 part of antimony. Music type, in addition, contains tin; and the common white metal used for teapots, under the name of *Britannia metal,* consists of equal parts of brass, antimony, tin, bismuth, and lead. The value of the antimony in these alloys depends upon the hardness which it communicates to the compounds, without rendering them inconveniently brittle, and to the expansion which it confers upon them in the act of solidification, so valuable in the case of type metal. Equal parts of antimony and lead, however, produce a brittle alloy. The compounds of antimony with zinc and with tin are hard, white, and brittle. A mixture of 12 parts of tin, 1 part of antimony, and a small quantity of copper, furnishes a ductile alloy, forming a superior kind of pewter. If lead be

substituted for copper in this alloy it is rendered brittle. Antimony also combines readily with copper, furnishing a hard alloy which takes a good polish, but which becomes paler and more brittle in proportion as the quantity of antimony is increased. If 7 parts of powdered antimony and 3 of iron filings be exposed in a covered crucible to a very high temperature, a brittle alloy is formed sufficiently hard to emit sparks when filed.

With zinc, antimony unites to form two definite alloys, which may be prepared by fusing the two metals together in the proper proportions. They may be crystallized by a method similar to that adopted in the case of sulphur by fusion (341). One of these ($SbZn_3$) crystallizes in long acicular prisms, which belong to the oblique prismatic system; it decomposes water rapidly at 212° with evolution of hydrogen. The other alloy ($SbZn_2$) crystallizes in broad plates which twin together on an octohedral face.*

In combination with bitartrate of potash, oxide of antimony forms a powerful and valuable medicine. The teroxide, when ground up with linseed oil, furnishes a pigment which is employed to some extent as a substitute for white lead: it is much less injurious to the health of those who use it than pigments which contain lead.

(713) *Extraction of Antimony.*—Antimony is a tolerably abundant substance, and is always extracted from its tersulphide, though it is frequently found alloyed with other metals, and is sometimes met with in the native state.

The sulphide of antimony usually occurs in a matrix of quartz, sulphate of baryta, and limestone. The *crude antimony* of commerce is merely the sulphide freed from the greater part of its earthy impurities. This purification is effected by placing the ore upon the bed of a reverberatory furnace, covered with charcoal-

* Mr. J. P. Cooke, who has studied these alloys minutely, finds that in each case the crystalline form of the alloy is preserved, although the proportions of the two metals may vary within considerable limits; thus, the form of needles, $Sb\,Zn_3$, which would require, if in atomic proportion, a per-centage of 55·7 of antimony, is still preserved, though the antimony may fall as low as 35·77 or may rise as high as 57·24; whilst the form of plates ($SbZn_2$) is observed without any variation in the angular measurements, although the quantity of antimony may fall as low as 64·57 or may rise as high as 79·42, though 65·07 would represent the true atomic proportion. It is true both the forms belong to the same crystalline system, but they do not appear to be derivable one from the other. Mr. Cooke suggests that these observations may throw an important light upon the cause of the hitherto unexplained variation in composition occasionally observed in minerals of the same crystalline form, the components of which are not isomorphous; and he proposes the term *Allomerism* to designate such variation in the proportions of the constituents of the crystalline compound without any essential change in the crystalline form, the varying constituents not being isomorphous with each other.

powder. The sulphide melts, the earthy impurities float, and the fluid portion is drawn off into an iron basin, and is afterwards cast into loaves or cakes. If it be desired to extract the metal, the sulphide thus purified is reduced to a coarse powder, and again placed upon the bed of a reverberatory furnace: the temperature may be gradually raised to dull redness, but must be moderated to prevent the mass from entering into fusion: in about 12 hours fumes cease to rise, most of the sulphur is expelled, and a red mixture of the teroxide and tersulphide of antimony remains. During this process copious vapours of sulphurous and arsenious acids are given off, accompanied by a considerable portion of oxide of antimony. It is stated that nearly 20 per cent. of the metal is lost during this operation. The roasted mass is now mixed with about one sixth of its weight of powdered charcoal, made into a paste with a strong solution of carbonate of soda, and heated in crucibles to bright redness; the metal collects at the bottom; above it is a scoria consisting chiefly of a double sulphide of sodium and antimony. This scoria is known in the arts as the *crocus of antimony*. The metal is remelted with the scoria, and is then fit for sale. 100 parts of sulphide yield about 44 parts of metallic antimony, so that in the whole process about three sevenths of the antimony are lost.

On the small scale the metal is most easily procured by taking 4 parts of the powdered sulphide, 3 of crude tartar, and $1\frac{1}{2}$ of nitre, mixing them intimately, and throwing the powder in small portions at a time into a crucible kept at a bright red heat. The quantity of nitre employed is insufficient to oxidize both the sulphur and the metal, and the sulphur being the more combustible element of the two is the first to undergo oxidation, whilst the metal melts and collects at the bottom, beneath the slag of sulphate of potash. Commercial antimony commonly contains arsenic, iron, and often small quantities of copper and lead.

In order to obtain antimony free from arsenic, Wöhler mixes intimately 4 parts of finely-powdered commercial antimony with 5 of nitrate of soda, and 2 of anhydrous carbonate of soda. The mixture is heated to redness in a Hessian crucible, and the antimony burns quietly at the expense of the oxygen of the nitrate. After the deflagration is complete, the crucible is covered, and the mass is kept for half an hour at a temperature sufficient to soften but not to fuse it, from time to time pressing it down with an iron spatula. It is removed from the crucible by means of a spatula, whilst still in a pasty condition, then pulverized and thrown into boiling water: the solution contains the arseniate of soda, whilst

the greater part of the antimoniate of the alkali remains undissolved, and is well washed with boiling water. From this antimoniate of soda the metal is extracted by melting it with half its weight of crude tartar. The product thus obtained is an alloy of antimony with potassium: it is broken into small pieces and thrown into water; a copious disengagement of hydrogen takes place, the potassium is oxidized and dissolved, and the alloy falls to powder. It still retains iron, and, sometimes, lead. One third of the mass is converted into oxide by means of nitric acid; this oxide is well washed with water, dried, and then incorporated with the powdered metal; the mass is again melted in a covered crucible, and pure antimony is obtained beneath a layer of fused oxide, which retains the oxides of iron and lead.

Mr. Gore (*Phil. Trans.*, 1848, p. 185) has described a remarkable modification of antimony which may be procured by electrolytic action, in the following manner:—Dissolve 1 part of tartar-emetic in 4 parts of the solution obtained by dissolving sulphide of antimony, nearly to saturation, in hydrochloric acid, and subject the solution to the action of two or three cells of Smee's battery. A metallic deposit having the colour and lustre of highly-polished steel, with a peculiar mamillated surface and an amorphous structure, is formed. Its specific gravity is about 6·55. The metal thus deposited retains 5 or 6 per cent. of terchloride of antimony, and if suddenly struck sharply, or heated, it undergoes a rapid molecular change attended with a rise of temperature amounting sometimes to 450°, accompanied by the disengagement of abundant fumes of terchloride of antimony. The heat evolved is sufficient to boil water or even to fuse small pieces of tin. After this change has occurred the metal is found to retain its cohesion, and its metallic aspect, but it becomes grey, and acquires a granular fracture, and an increased density. A corresponding substance may be obtained if terbromide be substituted for terchloride of antimony; the deposited metal in this case retaining bromide of antimony.

(714) Oxides of Antimony.—Antimony forms three well-marked oxides: the first is the most important, as it constitutes the basis of the antimonial salts employed in medicine. The oxides have the following composition:—

		Oxygen.	Antimony.
Teroxide	SbO_3	= 16·44	+ 83·56
Antimonic acid . . .	SbO_5	= 24·69	+ 75·31
Antimonious acid . . .	SbO_3,SbO_5	= 20·78	+ 79·22

Teroxide of Antimony, formerly called the *Sesquioxide* (SbO_3

= 146).—In the anhydrous state this oxide is found crystallized in prisms in a rare mineral called *white antimony ore,* of specific gravity 5·56. The anhydrous teroxide is best procured by boiling powdered metallic antimony to dryness in an iron ladle, with excess of strong sulphuric acid; an insoluble sulphate is formed, and sulphurous acid is disengaged. To remove the sulphuric acid, the residue is treated with carbonate of soda and is well washed: the greyish-white insoluble powder which remains is the teroxide. When heated it assumes a yellow colour, but recovers its whiteness on cooling. When heated in closed vessels it may be melted; at a high temperature it may be volatilized, and the vapour may be condensed in brilliant crystalline needles isomorphous with the unusual form of arsenious acid. Occasionally it crystallizes in octohedra, like the common variety of arsenious acid. In the open air it burns like tinder, and is converted into antimonious acid. Hydrochloric and tartaric acids dissolve it freely. Nitric acid converts it into one of higher oxides of antimony. With sulphuric acid it forms an insoluble sulphate, though its basic properties are but feeble. In the hydrated state it may be obtained by pouring a solution of terchloride of antimony into an excess of a solution of carbonate of soda. In this form it is readily soluble in solutions of potash and of soda; but the simple ebullition or evaporation of the liquid causes a separation of teroxide of antimony in prismatic crystals.

(715) *Antimonic Anhydride,* or *Antimonic Acid* ($SbO_5 = 162$).—This compound may be obtained by oxidizing the tersulphide with nitric acid, and expelling the excess of nitric acid by a heat below redness. It is of a pale yellow colour, is tasteless and insoluble in water. A strong heat expels one fifth of its oxygen, and converts it into the antimoniate of antimony (SbO_3, SbO_5), which is a white powder, often termed *antimonious acid,* but which possesses no acid characters; for if treated with bitartrate of potash it is decomposed, tartrate of antimony and potash (*tartar-emetic*), being formed, whilst antimonic acid is left.

Antimoniates.—Antimonic acid forms definite compounds with the alkalies: a boiling solution of potash dissolves it, and on the addition of an acid, the liquid deposits hydrated antimonic acid in the form of a white powder (SbO_5, 4 HO), which reddens litmus, and is freely soluble in cold solutions of the alkalies, and in hydrochloric acid. The hydrated acid may also be obtained by treating metallic antimony with nitric acid, or by decomposing the pentachloride of antimony with water. Fremy states that antimonic acid may, like binoxide of tin, be obtained in two modifications, each

of which combines with different amounts of base, and forms a distinct class of salts: to one of these modifications he gives the name of *antimonic acid;* its normal salt with potash has the formula ($KO, SbO_5 + 5 Aq$): the other modification he terms *metantimonic acid.* To the normal potash salt of the latter acid, he assigns the formula ($2KO, SbO_5$).

According to Fremy, antimonic acid is monobasic, but it is capable of forming both normal and acid salts. *Normal antimoniate of potash* may be procured by heating 1 part of metallic antimony with 4 parts of nitre in an earthen crucible. The white mass so obtained is powdered, and washed with warm water, to remove the excess of potash and nitrite of potash. The residue must be boiled in water for an hour or two; the *insoluble anhydrous* antimoniate is thus converted into a *soluble* hydrated modification consisting of $KO, SbO_5 + 5 Aq$. The insoluble residue now consists chiefly of biantimoniate of potash. The normal salt possesses the property of freely dissolving the biantimoniate, which is precipitated when such a solution is mixed with any neutral salt of one of the alkalies. The normal antimoniate does not crystallize, but forms a gummy mass, which has an alkaline reaction; it is readily decomposed by acids, including the carbonic, whilst the biantimoniate is deposited. When heated to 320° it loses 2 out of its 5 atoms of water, and becomes insoluble.

Biantimoniate of Potash ($KO, 2 SbO_5$) is obtained by transmitting a current of carbonic acid through a solution of the normal antimoniate. It is soluble in a hot solution of the normal antimoniate, and is deposited in crystals as the liquid cools.

If antimonic acid be heated with oxide of lead it combines with it and yields a yellow compound, which is used as a pigment under the name of *Naples yellow.*

(716) *Metantimonic Acid* ($2HO, SbO_5$).—This compound derives its principal interest from the circumstance of its yielding a soluble compound with potash, which may be employed as a test for soda. The *bimetantimoniate of potash* ($KO, HO, SbO_5 + 6 Aq$) is the salt which is used for this purpose. In preparing this compound, antimoniate of potash is first formed by deflagrating antimony with nitre, washing and boiling the residue in the manner already described, so as to bring the whole of the normal antimoniate into solution. The liquid thus obtained is filtered, and evaporated to a syrupy consistence in a silver dish; fragments of hydrate of potash are then added, and the evaporation is continued until a drop of the liquid placed upon a cold slip of glass begins to crystallize; it is then allowed to cool, and the alkaline supernatant liquid is poured

off the crystals, which are allowed to drain upon a porous tile. When the salt is required as a test for soda, 30 or 40 grains of this residue are to be washed quickly with about twice their weight of cold water, and allowed to subside; this washing is to be repeated two or three times, in order to remove traces of adhering potash: lastly, a little cold water is to be digested for a few minutes upon the residue, and the filtered liquid may be used to ascertain the presence of soda. The presence of free potash impairs the delicacy of the reaction. One great inconvenience which attends the use of this reagent is the circumstance, that if the solution be kept for a few days, the bimetantimoniate of potash passes spontaneously into the normal antimoniate, and this salt does not precipitate the compounds of soda; both salts contain exactly the same amount of acid and of base (KO,HO,SbO_5) = (KO,SbO_5,HO), the difference in properties being due to difference in the molecular constitution of the two salts. If the solution of bimetantimoniate be boiled, its conversion into normal antimoniate is effected in a few minutes. The *bimetantimoniate of soda* ($NaO, HO,SbO_5 + 6\,Aq$) is an insoluble salt, which crystallizes in octohedra.

(717) *Antimoniuretted Hydrogen* (H_3Sb?)—The composition of this gas is not known with certainty, for at present it has never been obtained free from hydrogen. It is inferred, however, to contain 3 atoms of hydrogen to one atom of the metal, because, when transmitted through a solution of nitrate of silver, a precipitate of antimonide of silver is formed, consisting of Ag_3Sb; $3(AgO,NO_5) + H_3Sb$ becoming $3(HO,NO_5) + Ag_3Sb$. Antimoniuretted hydrogen is formed by dissolving an alloy of zinc and antimony in diluted sulphuric acid. When any salt of antimony is poured into a mixture of zinc and sulphuric acid which is disengaging hydrogen, the antimonial salt becomes decomposed; one portion of the antimony is deposited in the form of a black powder upon the surface of the zinc, whilst another portion combines with the hydrogen, and assumes the gaseous state. It forms a colourless gas which is without any marked odour. When burned, it deposits white fumes of oxide of antimony, and if transmitted through a glass tube, heated to low redness, the gas is decomposed, and the antimony forms a brilliant metallic crust upon the heated portion of the tube.

(718) SULPHIDES OF ANTIMONY.—Two compounds of antimony with sulphur are known; the tersulphide (SbS_3), and the pentasulphide (SbS_5), corresponding to the teroxide and to antimonic acid. They are usually regarded as sulphur-acids, since they combine with the sulphides of the alkaline metals, and form definite salts.

Tersulphide of Animony ($SbS_3=170$; *Sp. Gr.* 4·6).—This substance constitutes the only ore from which the metal is obtained. The native sulphide, or *grey antimony ore*, is usually found in granite or slate rocks, and generally contains lead and arsenic, besides a variable amount of pyrites. The pure sulphide consists of 71·76 per cent. of antimony and 28·24 of sulphur. It occurs crystallized in four-sided striated prisms, which have a bluish-black colour, and a strong metallic lustre. It is friable, and melts below a red heat, crystallizing as it cools. It may be distilled unchanged in closed vessels, at a very high temperature, but by roasting in the open air it is converted into a fusible mixture of teroxide and tersulphide of antimony. This oxysulphide, after it has been fused, constitutes the commercial *glass of antimony*, which contains about 8 parts of the teroxide of antimony to 1 part of tersulphide. If the oxide be in excess, the glass is transparent, and of a fine red colour: the greater the proportion of the sulphide, the darker is the tint. The glass attacks the silica of the crucible in which the fusion is performed, and dissolves a considerable portion of it. A native *oxysulphide* of antimony ($SbO_3, 2SbS_3$, known as *red antimony ore*) occurs crystallized in oblique rhombic prisms.

The tersulphide of antimony may be obtained in crystals by melting together, at a red heat, a mixture of sulphur and teroxide of antimony; sulphurous acid escapes, and the tersulphide is formed, thus: $2\ SbO_3+9\ S=2\ SbS_3+3\ SO_2$.

A red amorphous anhydrous tersulphide may be obtained by boiling a solution of terchloride of antimony in hydrochloric acid with one of hyposulphite of soda. The anhydrous tersulphide may also be obtained of a beautiful orange colour, by transmitting sulphuretted hydrogen through a solution of any salt of the metal: on being heated in closed vessels, it assumes a dark metallic appearance, resembling that of the native sulphide. If heated in a current of hydrogen gas, the sulphur is removed and metallic antimony is left. The sulphide, whether artificial or native, is dissolved by hot hydrochloric acid, and furnishes a convenient source of pure sulphuretted hydrogen, provided that the gas be washed, to free it from traces of antimony and hydrochloric acid which it is apt to retain in suspension.

Tersulphide of antimony is readily soluble in solutions of the sulphides of the alkaline metals, and forms colourless compounds, which have been regarded as double sulphides, or *sulphantimonites*; a hot solution of the alkaline sulphide can dissolve much more of the sulphide of antimony than it can retain when cold; on the addition of an acid, the sulphide of the alkaline metal is decom-

posed, and the sulphide of antimony is reprecipitated. If sulphide of antimony in fine powder be boiled with a solution of carbonate of potash, or of caustic potash, it is dissolved; the filtered liquid on cooling deposits a reddish-brown substance, known as *kermes mineral*. This substance is not a definite compound, but is a variable mixture of tersulphide and teroxide of antimony, the latter being combined with a small portion of the alkali. The action of carbonate of potash on the sulphide is represented in the following equation:—

$$6(KO,CO_2)+3(SbS_3)=3(KO,2\,CO_2)+3\,KS+2SbS_3,SbO_3.$$

In this mixture of SbS_3 and SbO_3, H. Rose found crystals of teroxide of antimony, which were visible by the aid of the microscope. Bitartrate of potash, or diluted hydrochloric acid, dissolves out the teroxide, leaving the tersulphide. If to the liquid, after deposition of the kermes, hydrochloric acid be added, effervescence takes place, with escape of sulphuretted hydrogen, owing to the decomposition of sulphide of potassium, and the excess of sulphide of antimony which it retained is precipitated as the *golden sulphide of antimony*. This sulphide contains a larger proportion of sulphur than the tersulphide, from the gradual oxidation of the antimony in the solution before the precipitation is effected.

Pentasulphide of Antimony ($SbS_5=202$), or *Sulphantimonic Acid* as this compound is often termed, may be obtained by transmitting a current of sulphuretted hydrogen through an acid solution of pentachloride of antimony. It forms an orange-yellow precipitate, which is anhydrous, but is remarkable for the facility with which it combines with the sulphides of the alkaline metals. The tribasic *sulphantimoniate of sodium* ($3\,NaS,SbS_5+18\,Aq$), or Schlippe's salt, crystallizes in large and very brilliant transparent tetrahedra. It may be obtained in various ways: the easiest plan consists in thoroughly mixing 18 parts of finely-powdered tersulphide of antimony, 12 of dried carbonate of soda, 13 of quicklime and $3\frac{1}{2}$ of sulphur; the mixture is ground up with water, and placed in a well-closed bottle, which is completely filled with water; it is allowed to digest, with frequent agitation, for 24 hours; the clear liquid is filtered off, and allowed to evaporate spontaneously in a closed vessel over sulphuric acid. This salt when mixed with an acid deposits pure pentasulphide of antimony.

(719) CHLORIDES OF ANTIMONY.—Antimony has a powerful affinity for chlorine. It forms two chlorides, $SbCl_3$ and $SbCl_5$: they correspond in composition with the oxides and sulphides.

Terchloride of Antimony ($SbCl_3=228{\cdot}5$; *Sp. Gr. of Vapour*,

8·1; *Boiling pt.* 433°; Kopp).—This substance, from its ready fusibility, was formerly known under the name of *butter of antimony*. It may be obtained in the anhydrous form by distilling an intimate mixture of 8 parts of corrosive sublimate with 3 of powdered metallic antimony; calomel, terchloride of antimony, and an amalgam of antimony are formed; $2\ Sb+4\ HgCl=SbCl_3+SbHg_2+Hg_2Cl$. Terchloride of antimony may be more cheaply prepared by mixing sulphate of antimony with twice its weight of chloride of sodium, and then distilling the mixture. It may also be obtained by distilling the residue left on dissolving tersulphide of antimony in hydrochloric acid. The terchloride of antimony is a volatile, fusible, crystallizable compound, which is deliquescent, and powerfully corrosive in its action on animal tissues; it is soluble in hydrochloric acid, and in a small quantity of water; but if thrown into a large mass of water an insoluble oxychloride falls, which gradually assumes a compact crystalline form, consisting of $SbCl_3$, $2\ SbO_3$; it was formerly called *powder of algaroth*. On diluting a hot solution of terchloride of antimony in hydrochloric acid with hot water, it deposits, on cooling, brilliant needles, which may be represented as ($SbCl_3$, $5\ SbO_3$): by heat, the chloride is sublimed, leaving the oxide. Terchloride of antimony is used for bronzing gun-barrels, in order to prevent them from rusting.

Perchloride or *Pentachloride of Antimony* ($SbCl_5=299·5$) is prepared by exposing powdered antimony, gently heated in a retort, to a current of dry chlorine in excess. It forms a volatile, colourless liquid, which emits dense, suffocating, white fumes when exposed to the air. With a small quantity of water it forms white, deliquescent crystals; but it is decomposed by a large quantity oi water, and metantimonic acid, which retains a little hydrochloric acid, is deposited: $SbCl_5+5HO=SbO_5+5HCl$. Dry perchloride of antimony absorbs sulphuretted hydrogen, and forms with it a white crystalline fusible solid ($SbCl_3S_2$), which corresponds in composition to the chlorosulphide of phosphorus. Both the chlorides of antimony form definite compounds with ammonia. The perchloride of antimony is sometimes used as a chlorinating agent, since it readily parts with a portion of its chlorine to many compounds of organic origin which contain hydrogen.

The *terbromide* of antimony is a colourless crystalline solid. The *teriodide* is a solid of a red colour. *Tartar-emetic* (KO,SbO_3, $C_8H_4O_{10}+Aq$) is an important salt of antimony which is used in medicine; it will be described hereafter (1107).

(720) CHARACTERS OF THE COMPOUNDS OF ANTIMONY.—Ac-

cording to Péligot (*Ann. de Chimie*, III. xx. 297), teroxide of antimony forms salts which contain 1, 2, or 4 equivalents of acid. Most of them when largely diluted with water become milky from the deposition of a subsalt of sparing solubility; but this milkiness disappears on the addition of tartaric acid, or of bitartrate of potash. They are all of them colourless, and when taken internally in large doses, produce poisonous effects. Infusion of cinchona bark yields a copious insoluble precipitate with antimonial salts, and it has been recommended to exhibit this medicine in cases of poisoning with antimony: it is not however to be relied on.

Except when tartaric acid is present, the *caustic alkalies* give, with antimonial salts, a white precipitate soluble in excess of the alkali; *ammonia* and the *carbonates of the alkalies*, a white precipitate nearly insoluble in excess. But the characteristic reaction of these salts when in solution is the formation of an orange-coloured precipitate of hydrated tersulphide of antimony, when their solutions, acidulated with hydrochloric acid, are acted on by *sulphuretted hydrogen*; this precipitate is soluble in hydrosulphate of ammonia. In detecting antimony for medico-legal purposes, antimoniuretted hydrogen is first prepared, and subsequently decomposed by heat. In order to effect this, the suspected liquid, after boiling with hydrochloric acid and a little chlorate of potash, is filtered and introduced into Marsh's apparatus; the experiment is then proceeded with as directed for arsenic (709). The suspected solution may also be acidulated with hydrochloric acid, and boiled with a slip of bright copper foil, which becomes coated with a violet-coloured film of reduced antimony: when heated the antimony does not sublime in octohedra like arsenic; but the metal may be identified by heating the slip in a tube with a solution of pure potash, exposing the surface of the metal freely to the air; the antimony is gradually oxidized and dissolved. The solution should next be somewhat diluted, submitted to the action of sulphuretted hydrogen, filtered from any sulphide of copper or lead, and then on the addition of hydrochloric acid in slight excess the antimony is precipitated as sulphide in characteristic orange flocculi. This precipitate may be dissolved in hydrochloric acid, and will then give a crust of metallic antimony if introduced into Marsh's apparatus.

(721) *Estimation of Antimony.*—In determining the quantity of this metal, the solution is first acidulated with a mixture of hydrochloric and tartaric acid, then subjected to a current of sulphuretted hydrogen, and exposed for a few hours in an open, shallow dish, at a temperature not exceeding 100° F.: the excess of sulphuretted hydrogen is thus got rid of, and the whole of the

antimony is separated as sulphide, but the weight of the dried precipitated sulphide of antimony cannot be relied upon as furnishing a correct datum for estimating the metal, because it is liable to contain a variable excess of uncombined sulphur. It must therefore be dried at 212°, and weighed; a certain proportion of it is then dissolved in hot aqua regia, after which the solution is mixed with a little tartaric acid; and the sulphur, which has by this means been converted into sulphuric acid, is precipitated by the addition of chloride of barium: the sulphur is calculated from the weight of the sulphate of baryta obtained, and deducted from the weight of sulphide of antimony employed; the difference is estimated as antimony. According to Bunsen, the sulphide may be converted into antimonious acid (SbO_3,SbO_5), in which form it may be weighed by proceeding as follows:—place the sulphide in a counterpoised porcelain capsule, with a concave cover, moisten it with red concentrated nitric acid, and evaporate to dryness by the aid of a water-bath: the white mass of sulphate of antimony, which is left, is converted by ignition into antimonious acid, 100 parts of which correspond to 79·22 of the metal. The oxidation of the sulphide of antimony may also be effected by mixing it intimately with 40 or 50 times its weight of red oxide of mercury, and simply igniting the mixture in a covered crucible until it ceases to lose weight; sulphurous acid and metallic mercury are expelled, and antimonious acid is left as before. If the precipitate contain a large excess of sulphur it may be digested with bisulphide of carbon before proceeding to the oxidation. Antimony may be separated, by means of sulphuretted hydrogen, from all the metals previously described, with the exception of cadmium, tin, tungsten, molybdenum, and arsenic. Sulphide of cadmium is not soluble in hydrosulphate of ammonia, whilst that of antimony is soluble; this liquid may therefore be employed to separate these metals.

(722) In order to *separate arsenic from antimony*, Bunsen (*Liebig's Annal.*, cvi. 8) digests the mixed freshly-precipitated sulphides in bisulphite of potash. If the temperature be gradually raised to the boiling-point, the sulphide of arsenic is dissolved, and the sulphides of antimony and tin, if the latter be present, are left behind; the solution contains arsenite and hyposulphite of potash produced by the following reaction:—

$$2\,AsS_3 + 8(KO, 2\,SO_2) = 2\,(KO,AsO_3) + 6\,(KO,S_2O_2) + S_3 + 7\,SO_2.$$

The same object may be attained by dissolving the sulphides in a solution of sulphide of potassium, diluting with water, treating

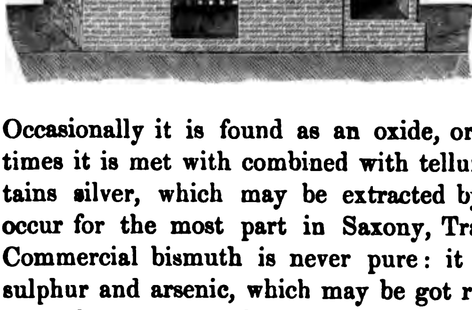
with sulphurous acid gas, and boiling the liquid. The sulphides of antimony and tin are precipitated, and the arsenic can be thrown down from the filtrate by means of sulphuretted hydrogen.

The *separation of antimony from tin* in a metallic alloy may be effected with tolerable accuracy, by dissolving the alloy in hydrochloric acid, which is to be mixed with a small proportion of nitric acid, in order to prevent loss of antimony as antimoniuretted hydrogen. The two metals are then precipitated together by means of metallic zinc, and the pulverulent metals are weighed. This precipitate is redissolved in weak aqua regia, and is digested at a gentle heat upon a bar of tin, which throws down antimony only. The precipitated metal is collected, washed, dried, and weighed.

§ IX. Bismuth (Bi=210). *Sp. Gr.* 9·799.

(723) Bismuth is not an abundant metal: it occurs generally in the native state in quartz rock, and is extracted from its matrix by simple fusion, the mineral being usually heated in iron tubes, which are placed across the furnace in an inclined position; the ore is introduced at the upper end, and the melted metal is drawn off into iron basins below, by opening a plugged aperture at intervals. Fig. 331 shows a section of the furnace used at Schneeberg in this operation, where the bismuth is extracted from an ore rich in cobalt.

Fig. 331.



Occasionally it is found as an oxide, or as a sulphide, and sometimes it is met with combined with tellurium. It generally contains silver, which may be extracted by cupellation. Its mines occur for the most part in Saxony, Transylvania, and Bohemia. Commercial bismuth is never pure: it is apt to contain a little sulphur and arsenic, which may be got rid of by fusing the metal with about one tenth of its weight of nitre; but it still retains silver, lead, and iron. It may be obtained free from these impurities by solution in nitric acid: the acid liquid when saturated with the metal is allowed to become clear, and is poured into a large bulk of water. A sparingly soluble subnitrate of bismuth is thus

precipitated: it is washed, dried, and reduced by ignition with one tenth of its weight of charcoal, in a crucible: pure bismuth collects at the bottom.

Properties.—Bismuth is a hard, brittle metal of a reddish-white colour; it fuses at 507°, according to Rudberg, or 513°, to Person, and it expands considerably at the moment of congelation: when pure it may be obtained by slow cooling after fusion (69) crystallized in large cubes,* which are frequently hollow. Marchand and Scheerer found that the density of bismuth was diminished by powerful compression, probably owing to the formation of minute internal fissures; they thus reduced it from 9·799 to 9·556. Bismuth is slightly volatile when strongly heated. It is but little altered by exposure to the air at ordinary temperatures, but is rapidly oxidized if exposed to the air at a red heat; if thrown in powder into chlorine it takes fire: it also unites easily with bromine, with iodine, and with sulphur. Hydrochloric acid has little action it. Boiling sulphuric acid oxidizes it with evolution of sulphurous acid; but its proper solvent is nitric acid, which oxidizes and dissolves it rapidly.

Uses.—The applications of bismuth are but limited; it is occasionally employed instead of lead in cupellation: some of its compounds are used as pigments, and the subnitrate is employed medicinally. Its most remarkable alloy is that known as *fusible metal.* This is composed of 2 parts of bismuth, 1 of lead, and 1 of tin, or 1 atom of bismuth, 1 of lead, and 2 of tin. The mixture fuses at a little below 212°: passing through a pasty condition previous to complete fusion. It dilates in an anomalous manner, when exposed to heat; according to Erman it expands regularly from 32° to 95°, then contracts gradually to 131°, at which point it occupies a less bulk than it did at 32°; it then expands rapidly till it reaches 176°, and from that point till it melts its expansion is uniform. This faculty of expanding as it cools, while still in the soft state, renders the alloy very valuable to the die sinker, who employs it to test the perfection of his die,—every line being faithfully reproduced on taking a cast.

Bismuth increases the fusibility of those metals with which it is alloyed, to a remarkable extent.

(724) Oxides of Bismuth.—Bismuth forms two principal oxides, a teroxide (BiO_3), and an acid oxide (BiO_5); besides these there is a compound oxide (BiO_3,BiO_5), formed by the union of

* The crystals of bismuth, however, belong to the rhombohedral system, as they are not true cubes, but rhombohedra, the angles of which are within 2° 20′ of right angles.

the two preceding combinations. A binoxide (BiO_2) of a brown colour was also obtained by Schneider: it burns into the teroxide when heated in the air.

Teroxide of Bismuth ($BiO_3=234$); *Sp. Gr.* 8·211.—This compound may be obtained in the anhydrous form, by heating the nitrate or the subnitrate of the metal to low redness. It is a yellow, insoluble powder, which fuses at a red heat, and is easily reduced to the metallic state by heating it with charcoal. A white hydrate of this oxide (BiO_3,HO) may also be procured by precipitating a salt of bismuth by an excess of ammonia.

Peroxide of Bismuth, or *bismuthic acid* ($BiO_5=250$), may be procured by digesting the washed hydrated teroxide of bismuth in a concentrated solution of potash, and transmitting chlorine gas. A blood-red solution of bismuthate of potash is thus obtained, and a red precipitate is formed, which is to be well washed, and then digested in cold nitric acid to remove the oxide of bismuth with which it is always mixed. A red powder is thus left, which is hydrated bismuthic acid (HO,BiO_5); by a heat of 270° it is rendered anhydrous, and assumes a brown colour. At a somewhat higher temperature it loses oxygen, and becomes converted into the intermediate oxide, or bismuthate of bismuth. According to Arppe more than one of these intermediate oxides may be formed. Bismuthic acid combines with the alkalies, but these compounds are decomposed by mere washing with water. The acid is decomposed by concentrated sulphuric acid at ordinary temperatures, and by nitric acid if the temperature be raised, oxygen being expelled and a salt of the teroxide formed.

(725) Tersulphide of Bismuth ($BiS_3=258$) occurs native as *bismuth glance* in delicate needles, and in crystals isomorphous with those of tersulphide of antimony. It may be formed artificially by fusing the metal with sulphur: a fusible dark grey compound, with a feebly metallic lustre, is thus obtained; in closed vessels it is decomposed into a subsulphide, and into free sulphur, which distils; in the open air sulphurous acid escapes, and teroxide of bismuth remains. When solutions of bismuth are treated with sulphuretted hydrogen, a black precipitate of tersulphide of the metal is formed. Tersulphide of bismuth is dissolved by the metal in all proportions, a circumstance which affords an easy method of obtaining it in crystals, since the tersulphide crystallizes at a temperature at which the metal still remains fluid.

(726) Terchloride of Bismuth ($BiCl_3=316·5$) may be obtained by heating bismuth in chlorine, or by mixing the metal in fine powder with twice its weight of corrosive sublimate, and dis-

tilling. It is a very fusible, volatile, deliquescent compound; but is decomposed by a large quantity of water into free hydrochloric acid, and an oxychloride of bismuth ($BiCl_3$, 2 BiO_3+6 Aq), known under the name of *pearl white*. This compound is insoluble in tartaric acid, in potash, and in hydrosulphate of ammonia, characters which distinguish it from the corresponding compound of antimony.

TERIODIDE OF BISMUTH (BiI_3) is obtained by heating in closed vessels 2 parts of bismuth with 13 of iodine; it sublimes in six-sided, brilliant plates. It is readily fusible, is of a dark brown colour, and is insoluble in water; but it forms soluble compounds with hydrochloric acid, and with iodide of potassium.

(727) *Nitrate of Bismuth* (BiO_3,3 NO_5+9 Aq); *Sp. Gr.* 2·376. —This salt is the only other soluble compound of bismuth of any importance, and is easily procured by dissolving the metal in nitric acid: it may be crystallized from the acid solution in large transparent prisms. If the solution, not too strongly acid, be largely diluted with water, an acid salt remains in the solution, and *subnitrate* falls, composed of (5 BiO_3, 4 NO_5+9 HO; Becker); it was called by the old writers *magistery of bismuth.*

(728) CHARACTERS OF THE SALTS OF BISMUTH.—Bismuth when in solution presents characters less marked than many metals. Its salts are colourless unless the acid be coloured; they are poisonous in large doses; its solutions have an acid reaction; when diluted they become milky, owing to the formation of sparingly soluble subsalts, unless a large excess of acid be present. *Iron, zinc, copper,* and *tin* throw down bismuth from its solutions in the metallic state. The *alkalies* give a white precipitate of the hydrated oxide, which is insoluble in excess of the precipitant, and becomes yellow by boiling it with the liquid. Solutions of the *carbonates, phosphates, tartrates,* and *ferrocyanides* give white precipitates with its salts. Phosphate of bismuth is insoluble in diluted nitric and acetic acids, and it has in consequence been proposed by Chancel as a convenient form in which phosphoric acid may be precipitated from acid solutions (370). This phosphate is, however, largely soluble in hydrochloric acid, whilst if sulphuric acid is present the precipitate generally becomes contaminated with basic sulphate of bismuth. *Sulphuretted hydrogen* throws down a black sulphide of bismuth, which is insoluble in hydrosulphate of ammonia. *Chromate of potash* gives a yellow precipitate of chromate of bismuth, which is insoluble in caustic potash, and is thus distinguished from chromate of lead. *Before*

the blowpipe its salts are easily reduced on charcoal, and yield a brittle bead of bismuth, around which the yellow oxide is deposited.

(729) *Estimation of Bismuth.*—Bismuth is estimated in the form of the teroxide, 100 parts of which correspond to 89·74 of the metal. Carbonate of ammonia is its best precipitant, but the solution must not contain any chloride or hydrochloric acid, as an oxychloride of bismuth would in that case be precipitated and a portion of the bismuth would be volatilized with the chlorine on ignition; the metal must in such a case be precipitated in the form of sulphide. It may be separated from the alkalies, from titanium, and from all the metals of the first four groups (with the exception of cadmium), by means of sulphuretted hydrogen; the solution having been first acidulated with acetic acid. From tin, and from the metals of the fifth group, it may be separated by digesting the mixed sulphides (obtained by transmitting sulphuretted hydrogen through the liquid) in hydrosulphate of ammonia, which leaves the tersulphide of bismuth, and dissolves the other sulphides. The sulphide must be dissolved in nitric acid, and precipitated by carbonate of ammonia, which after standing for a few hours throws down the whole of the bismuth in the form of carbonate: it must be ignited in a porcelain crucible; the carbonic acid is thus expelled, and the teroxide of bismuth remains.

Bismuth may be separated from cadmium by the addition of ammonia in excess to the solution of the sulphides in nitric acid; the cadmium is retained in solution, whilst the bismuth is precipitated.

CHAPTER XVI.

§ I. Copper ($Cu=31·7$). *Sp. Gr. from* 8·921 *to* 8·952.

(730) The ores of copper are numerous. The metal is frequently found native, crystallized in cubes, octohedra, or dendritic crystals; or else in masses, as in the North American and Siberian mines. In the neighbourhood of Lake Superior there is a vein of massive native copper, associated with silver; this vein is in many parts 2 feet in thickness. The most common ore of copper however is the copper pyrites, or mixed sulphide of copper and iron (Cu_2S, Fe_2S_3), which occurs in the primitive rocks, and especially in the *killas*, or clay-slate. More rarely the pure subsulphide of copper (Cu_2S) is found in the mines of Cornwall and of the Ural Moun-

tains. Other less abundant ores are the blue and green carbonates, and the red and black oxides of copper.

The Cornish mines furnish more than a third of the copper which is smelted in Great Britain, but considerable supplies of ore are received from Chili, Cuba, and South Australia. The most important seat of the copper smelting is Swansea, which sends forth annually from 18,000 to 20,000 tons of the refined metal. North America and Saxony supply the larger portion of the remainder. The Australian ore consists chiefly of the green and blue carbonate in a siliceous matrix; these ores contain from 25 to 35 per cent. of copper. Cuba furnishes both the oxides and the sulphides of the metal. Many of the ores from Chili are valuable on account of the large proportion of silver which they contain. The Cornish copper pyrites usually occurs (mixed with small quantities of oxide of tin and arsenical pyrites) in a matrix of quartz, fluor-spar, and clay.

(731) *Extraction.*—The main object in the treatment of such an ore as the Cornish, is to oxidize and remove the sulphur and arsenic in the form of sulphurous and arsenious acids, and to get rid of the quartz and oxide of iron in the form of a fusible slag, composed of silicate of iron combined with other earthy impurities, leaving metallic copper free from admixture.

After the ore has been raised from the mine it is sorted; the purest portions are broken into small pieces of the size of a hazel nut, and the earthy portions are crushed and sifted, as in washing tin ore. The English ore is usually so mixed that it may contain an average of $8\frac{1}{2}$ per cent. of copper.

The theory of copper smelting as practised at Swansea, like that of many other operations in the arts, is simple, though the working details have the appearance of being complicated.* The principal processes may, however, be enumerated as follows:—

1. Calcining the ore.
2. Melting and granulating for coarse metal.
3. Calcination of the coarse metal.

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* The apparent complication of the process arises from one of its great practical merits—viz., from the circumstance that it admits of being modified to suit almost every variety of ore, and these modifications necessarily tend to increase its complexity. Le Play enumerates six principal varieties of ores as being wrought by this method.—1. Pyritous ores, containing from 3 to 15 per cent. of copper. 2. Richer ores of the same kind, yielding from 15 to 25 per cent. of copper. 3. Siliceous oxides of copper, yielding from 12 to 20 per cent. of metal. 4. Oxides and carbonates with subsulphide of copper, in a siliceous matrix. 5. Very pure siliceous sulphides of copper and iron, yielding from 10 to 15 per cent. of copper; and 6. Pure sulphides and oxides of copper, containing from 60 to 80 per cent. of the metal.

4. Melting for fine metal.
5. Roasting of the fine metal.
6. Refining and toughening.

We shall make a few remarks upon each of these processes in succession.

(732) 1. *Calcining the Ore.*—The calcination is conducted in large reverberatory furnaces, upon quantities of about 3 tons at a time; the heat is moderate, so as to avoid fusing the mass, which is spread evenly over the floor of the furnace, and stirred at intervals of 2 hours: this roasting is continued for 12 hours, at the end of which time the mass is converted into a black powder containing sulphide of copper, oxide and undecomposed sulphide of iron, and earthy impurities. Oxygen has a stronger affinity for iron than for copper, but the affinity of sulphur for copper is greater than for iron; and the effect of the roasting is seen in the production of oxide of iron and sulphurous acid, whilst the sulphide of copper remains unacted upon. During this and the subsequent processes, abundant white deleterious fumes are given off; containing arsenious, sulphurous, sulphuric, and hydrofluoric acids, and a certain portion of metallic arsenic. These fumes hang like a dense canopy over the smelting works and their vicinity: the cloud of *copper smoke*, as it is called, may be discerned at the distance of many miles.

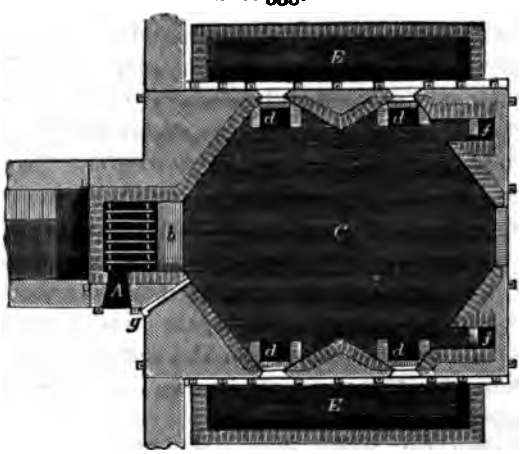
The *calcining furnace* employed in Wales is shown in section in fig. 332, and a plan of the hearth is exhibited in fig. 333. A is the fireplace: *b*, the bridge; *c c*, the hearth or roasting bed; *d d* are apertures in the floor, through which, by withdrawing an iron slide, the charge can be allowed to pass into the *cub*, or vault, E, when the roasting is complete; *f*, *f* are the flues; *g* is an opening for the admission of air to the hearth; H, H are hoppers for charging the furnace, and *t*, a platform over which the barrows of ore are conveyed to the hoppers.

The fuel used in roasting the ore is chiefly anthracite, a coal which, under ordinary management, yields no flame. Flame, however, is absolutely necessary to the proper roasting of the copper ore: experience has taught the copper smelter to obtain this desideratum by limiting the supply of air to the fuel in the fire-grate, thus causing the carbonic acid which is formed at the lower part of the fire to be converted into carbonic oxide. By a nice adjustment of the supply of air through *g*, the other apertures of the furnace being closed, the carbonic oxide is gradually burned as it plays over the ore upon the hearth, *c c*; the maximum of heat is thus obtained at the minimum cost of fuel, the carbonic oxide

being completely burned before it reaches the flue. An admirable analysis of this operation is given by Le Play in his elaborate memoir on the Welsh method of copper smelting (*Ann. des Mines*, IV. xiii. 128).*

FIG. 332.

FIG. 333.



(733) 2. *Melting for Coarse Metal.*—The roasted ore is now subjected to fusion in the *ore furnace* with certain proportions of slag, the produce of a subsequent operation, of siliceous ore free from sulphur, and of fluor-spar if necessary: by this means the charge is converted into a fusible slag, consisting chiefly of silicate

* The heat emitted during the combustion of anthracite is very intense, so that it causes a rapid oxidation of the fire-bars of the furnace. This fuel has also the inconvenience of splitting into small fragments, which choke the air-ways between the bars, if the heat be suddenly applied. The copper smelter overcomes these difficulties by employing a grate consisting only of a few bars, which do not come into contact with the fuel itself, but only serve as a support for the clinker produced during the combustion of the coal. A bed of clinkers, 12 or 16 inches thick, rests upon the fire-bars, and above this the fuel is burned: from time to time the fireman removes portions of the clinker as it accumulates (Le Play).

of iron, and into sulphides of copper and of iron, which sink through the slag, and form what is termed a *matt*. This fusion occupies about 5 hours, each charge containing about 1½ ton of roasted ore. The matt thus procured contains about 33 per cent. of copper: it is run off while liquid into water, by which it is granulated. The product goes by the name of the *coarse metal*. The slag which floats above the matt is raked out of the furnace at a separate aperture. It ought to contain no appreciable quantity of copper.

3. *Calcination of the Coarse Metal.*—The granulated metal is again roasted for 24 hours, during which operation a large proportion of the sulphide of iron is converted into oxide.

4. *Melting for Fine Metal.*—A second fusion is performed upon this calcined matt with the addition of a portion of copper ore known to be rich in oxide of copper and in silica, and to contain but little iron pyrites. By this means the oxide of iron is removed in the form of a fresh slag of silicate of iron, and the oxygen contained in the freshly added oxide of copper completes the oxidation of any portion of sulphide of iron still remaining; the oxide of copper and the whole of the sulphide of this metal being reduced to the state of disulphide of copper (Cu_2S) or *fine metal*. The slags from this process, and all the subsequent ones, are preserved. This matt contains about 80 per cent. of copper. It is cast into pigs. The lower part of these pigs often contains a considerable quantity of tin, and, the alloy being the heavier, it sinks to the bottom. If a very pure metal be required, the upper parts of the pigs are detached from the lower portions, and the metal extracted from the upper portions of the ingots is known in the market as *best selected copper*.

5. *Roasting for Blistered Copper.*—The metal is now to be freed from the sulphur, which has hitherto been useful by forming a fusible compound with the copper, thus facilitating its separation from the impurities by which it was accompanied. With this view the pigs of fine metal are next subjected, for several hours, upon the bed of a reverberatory, to a heat just short of that required to fuse them; the metal by this means becomes oxidated at the surface, and a part of the sulphur which it still retains is oxidized; at last it is fused: a remarkable reaction then begins to take place. When oxide of copper and sulphide of copper are heated together, they mutually decompose each other; sulphurous acid and metallic copper are liberated; $Cu_2S + 2\,CuO = SO_2 + 4\,Cu$. It is not desirable that the temperature should be too strongly raised, as the oxide of copper would then combine with the silica still present in

the mass, and would cease to exert its oxidizing influence. After the charge has become liquid, the temperature of the furnace is therefore allowed to fall; the melted mass solidifies upon its surface, and an appearance of violent ebullition is produced from the formation of sulphurous acid gas, and its efforts to escape from the tenacious mixture: when this ceases, the desulphuration is complete. The heat is now rendered very intense, the copper melts, and sinks to the bottom, and separates completely from the slag, which consists chiefly of silicate of copper; the reduced metal is then run off into sand moulds. The ingots thus obtained, being full of bubbles, are termed *pimple* or *blistered copper*.

(734) 6. *Refining*, or *Toughening*.—The blistered copper now undergoes the concluding operation of refining. From 7 to 8 tons of the metal are placed in a reverberatory furnace and kept in a melted state for upwards of 20 hours, in order to oxidate the last traces of foreign metals: during this process a large quantity of oxide of copper is formed; part of this oxide is absorbed by the melted metal, and the copper, if examined at this stage, is found to be of a dull red colour, coarse grained and brittle. To reduce this oxide, the slags are skimmed off, and the surface is covered with a few shovelfuls of anthracite or of charcoal; the metal is then subjected to the process of *poling*, in which the trunk of a young tree is thrust into the molten metal. The inflammable gases disengaged from the green wood as it chars, produce a powerful agitation of the whole mass, and in about 20 minutes the poling is finished. The reducing influence of the combustible gases has in the meantime been brought to bear upon every portion of the melted metal. In this way the oxide diffused through the mass is deprived of oxygen. If the poling be carried too far, the copper again becomes brittle, and is said to be *overpoled*. This defect may be remedied by exposing the surface of the melted metal to a current of air. If too little poling be used, the metal is still brittle, and it is then said to be *underpoled*. The progress of the poling, therefore, requires careful watching: the refiner tests the metal from time to time by dipping a small test ladle into the melted mass; a sample of copper is thus removed, and cooled suddenly by immersion in water: the grain of the copper is judged of, by cutting the hammered button partially through with a chisel or shears, and then bending it by placing it in a vice. If properly refined, the broken surface will display a fibrous structure with a beautiful silky lustre. If underpoled, the fracture will be granular, with a number of red points. If overpoled, the fibres become coarser, and the fracture has a strong metallic lustre, but the silky

appearance is wanting. When upon testing, the copper appears to be fine grained, fibrous, and silky, of good colour and malleable, it is either ladled out and cast into ingots, or is cooled suddenly at the surface, by allowing water to run upon it; *rose copper* is thus produced, and successive films are thus made and removed till all the metal is consumed. There appears to be no doubt that the brittleness of underpoled copper is due to the presence of red oxide of copper in the metal, and Mr. Vivian has suggested that overpoled copper may be defective from the presence of a little carbon. Percy, however, was unsuccessful in the attempt to discover carbon in overpoled specimens.

The slags from the various operations are carefully remelted, and the copper which is extracted from them is termed *black copper*; it is run into pigs, which are subsequently refined.

The presence of a small quantity of tin in the refined copper is considered to be advantageous, as the toughness and tenacity of the metal are thereby increased. Antimony is singularly injurious; so small a quantity as 10 ounces in the ton, renders copper unfit for making brass that is required for rolling; and minute traces of nickel are also said greatly to injure the tenacity of the metal.

(735) In the Hartz, and in many mines where the ores contain a large quantity of sulphide of iron, and only about 4 per cent. of copper, the crude mineral is roasted in enormous heaps in the open air. These heaps are in the form of a truncated square pyramid, the base of which is about 30 feet square (340). The roasting is a very slow operation, requiring from 5 to 6 months for its completion. Spring and autumn are the most favourable seasons in which to commence it. The roasted ore is then subjected to processes not essentially differing from those already described.

In many copper mines the water which is pumped up is impregnated with sulphate of copper derived from the oxidation of the sulphide by exposure to the air: the copper is easily separated in the metallic form, by collecting the water in tanks containing scrap-iron: the iron unites with the oxygen and the acid, whilst the copper is set at liberty: $CuO,SO_3 + Fe = FeO,SO_3 + Cu$.

When the ore consists of the oxides and carbonates of copper, it is easily reduced to the metallic state by simple fusion with coke or charcoal; the copper is rendered tough by a process analogous to that of poling.

The copper of commerce is often very nearly pure. It contains minute quantities of arsenic, of iron, of lead, and sometimes of tin and silver. Copper may be readily obtained in a state of perfect

purity, by decomposing a solution of sulphate of copper by means of the voltaic battery: it is then deposited in coherent plates upon the negative electrode.

(736) *Properties.*—Copper is one of the metals which has been longest known to man: before the art of working iron was understood, it was in extensive use, either alone or alloyed with tin, for many of the purposes to which iron is now applied. It is of a well-known red colour, and has a peculiar, disagreeable odour and taste when moistened and rubbed. It is rather a hard metal, very tenacious, ductile, and malleable; after it had been melted beneath a layer of common salt, to exclude atmospheric air, pure copper was found by Scheerer and Marchand to have a sp. gr. of 8·921: the density was increased by hammering, and when drawn into fine wire it was obtained as high as 8·952: Daniell estimated its fusing point at 1996° F. If exposed to a very intense heat, it is capable of volatilization, but it is usually considered to be fixed in the fire. By slow voltaic action it may be obtained crystallized in cubes and octohedra, and is sometimes found native in these forms. It ranks among the best conductors of heat and electricity. If heated to redness in the open air, copper combines with oxygen rapidly, a layer of oxide is formed upon the surface, and as the oxide contracts more slowly than the metal beneath, it scales off if suddenly cooled, leaving a bright, clean, metallic surface. Exposure to a moist air at ordinary temperatures has no effect upon copper; neither has pure water; but in sea water, or in solutions of the chlorides, it is gradually corroded with the formation of an oxychloride of copper. Finely divided copper becomes ignited when touched with a glowing coal, and burns like tinder, being converted into the black oxide. Chlorine attacks the metal, which when in the form of leaf takes fire in the gas spontaneously. Nitric acid oxidizes and dissolves the metal with rapidity. Oil of vitriol does not act upon it in the cold, but if heated with it, the acid is decomposed, sulphurous acid being evolved and oxide of copper formed, which unites with the excess of acid to form the sulphate (343). Hydrochloric acid with access of air dissolves it: but if air be excluded, it has no such effect at ordinary temperatures; though if boiled upon the finely-divided metal, it dissolves it very slowly, and hydrogen is evolved (Odling). Copper also decomposes hydrochloric acid gas when heated in it to redness, subchloride of copper being formed and hydrogen separated. The fixed alkalies have little action on copper, but ammonia gradually dissolves the metal if the air has access to it, slow oxidation taking place. Before the oxyhydrogen blowpipe it burns with a green flame, and

if introduced into a flame of gas or of alcohol it communicates to it a green colour.

Uses.—The applications of copper in the arts are very numerous. Independent of its use in coinage, vast quantities of it are annually consumed in the sheathing of ships* and in the manufacture of boilers, and of various utensils for domestic purposes. It also forms the basis of a number of valuable alloys in extensive use: with zinc it furnishes the different varieties of brass; and with different proportions of tin, it forms bronze, bell-metal, gun-metal, and speculum-metal (676); whilst its oxides and salts are largely employed as pigments, and yield articles of some importance in the materia medica.

An alloy of copper and silicon containing 12 per cent. of the latter may be obtained by fusing together 6 parts of silicofluoride of potassium, 1 part of sodium and 1 of copper turnings: it is hard, brittle, and white, like bismuth. Another alloy with 48 per cent. silicon is of a fine bronze colour. It is as fusible as bronze, very ductile, and yields a wire a little softer than iron, but quite as tenacious: it may be worked well at the lathe.

(737) *Brass.*—The combination of zinc with copper has a well-known yellow colour, the tint of which becomes paler in proportion as the quantity of zinc is increased. A curious observation upon this point was made by Mr. D. Forbes, who found that a brittle crystalline alloy of a silver-white colour may be formed, containing 53·49 per cent. of zinc, and consisting of 7 equivalents of copper and 8 of zinc; but if the quantity of zinc were either increased or diminished, the alloy had the usual yellow colour of brass. The specific gravity of brass is greater than the mean of that of the metals which form it. Ordinary brass has a sp. gr. of 8·29; it contains about 64 per cent. of copper, being nearly Cu_2Zn. Brass which contains 25 per cent. of zinc melts at 1750° (Daniell), and a larger proportion of zinc increases its fusibility. By exposure to a long-sustained high temperature in closed vessels, the whole of the zinc may be expelled, and it is not possible to fuse the alloy without losing a portion of the zinc. The alloys of zinc and copper are malleable when cold, but are generally brittle when hot. An alloy largely used under the name of *Muntz metal,* or *yellow metal,* for the sheathing of ships, may be rolled whilst hot: it contains 2 equivalents of zinc to 3 of copper, or 60 per cent. of copper. The addition of about 2 per cent. of lead to brass im-

* Percy's experiments appear to show that the presence of a small quantity of phosphorus in the copper has some effect in protecting the metal from the corrosive action of sea water.

proves its quality if it is to be used at the lathe: it diminishes its toughness, and prevents it from hanging to the tool and clogging the file; but if intended for wire, the presence of lead must be avoided. A very small proportion of tin, even if it does not amount to 1 part in 200, greatly increases the hardness of the alloy. The ordinary *hard solder* for brass is an alloy consisting of 2 parts of brass and 1 of zinc. Brass is usually made by melting granulated copper in crucibles with rather more than half its weight of zinc: formerly a mixture of calamine and charcoal was substituted wholly or partially for metallic zinc. At Swansea, the Muntz metal is prepared by melting the two metals in a reverberatory furnace, which enables a large quantity of the alloy to be prepared with rapidity: but the process is attended with a considerable waste of zinc. The bronze used for coin is an alloy of 100 parts of copper with 5 of tin, or with 4 of tin and 1 part of zinc.

(738) OXIDES OF COPPER.—There are two salifiable oxides of copper, both of which are found in the native state; viz., the red oxide or suboxide (Cu_2O), which contains 88·8 per cent. of copper and 11·2 of oxygen, and the black oxide (CuO), which is the basis of the ordinary salts of the metal. It contains 79·85 per cent. of copper and 20·15 of oxygen. Some indications have been obtained of the existence of a still higher oxide, probably Cu_2O_3.

The *suboxide*, or *dioxide* ($Cu_2O = 71{\cdot}5$; *Sp. Gr.* 5·60), occurs native, crystallized either in the octohedron, or in some of its derived forms, or else in capillary crystals or in lamellar masses. There are various ways of obtaining this oxide artificially; one of the best consists in boiling the dibasic acetate of copper with sugar; the oxide of copper contained in the salt is thus deprived of half its oxygen, and the red oxide is deposited in small octohedra. It may also be procured by igniting 5 parts of powdered black oxide of copper with 4 parts of copper filings, in a covered crucible. The red oxide fuses at a full red heat. By decomposing the subchloride of copper with potash it is obtained as an orange-yellow hydrate ($4\,Cu_2O + Aq$; Mitscherlich). In this condition it combines with acids. A sulphate as well as a carbonate and an acetate of this oxide appear to exist. The salts of the suboxide of copper are unstable, and absorb oxygen readily. Some of its double salts are more stable: a *sulphite of copper and potash* [$Cu_2O,SO_2 + 2(KO,SO_2)$; Muspratt] may be obtained as a yellow insoluble precipitate, by mixing solutions of sulphite or of bisulphite of potash with sulphate of copper; part of the sulphurous acid being oxidized at the expense of half of the oxygen of the black oxide of copper.

The anhydrous oxide is resolved by most of the stronger acids into a salt of the black oxide, and into metallic copper. Nitric acid converts it into protoxide and dissolves it: hydrochloric acid converts it into the subchloride, which is soluble in excess of the acid. Hydrated suboxide of copper is soluble in a solution of ammonia, forming with it a colourless liquid. This solution is an extremely delicate test of the presence of oxygen in a gaseous mixture; a mere trace of oxygen causes it to assume a blue tint from the formation of the black oxide of copper, which when dissolved in solution of ammonia has an intense blue colour. The principal employment of suboxide of copper is in the manufacture of stained glass, to which it imparts a beautiful ruby or purple colour.

(739) *Black Oxide of Copper* ($CuO = 39 \cdot 7$; *Sp. Gr.* 6·4). —This oxide is a compound of considerable importance to the chemist. It is employed largely as a means of furnishing oxygen to organic substances in the regulated combustion by means of which their composition is determined (904). The best process for obtaining the black oxide of copper consists in dissolving copper in pure nitric acid, and decomposing the resulting nitrate in an earthen crucible, by the application of a red heat: the water and the nitric acid are thus expelled, and the black oxide remains behind in a state of purity: the heat should be long continued, but not too violent; otherwise the oxide sinters together and concretes into hard masses, which are pulverized with difficulty. A very pure oxide is also furnished by the decomposition of the carbonate by heat; or still more simply by heating a plate of copper to redness in a brisk current of air, and suddenly quenching it in water, in which case the oxide separates in black scales. It may be obtained as a hydrate of a light blue colour ($CuO, 2\,HO$), from any of its salts, by the addition of potash in excess; when boiled with water it becomes black and anhydrous. This hydrate is soluble in ammonia, a crystalline compound, containing $CuO, 2\,H_3N + 4\,HO$, being deposited from the liquid. The solution of the oxide in excess of ammonia is of a splendid blue colour: if slips of metallic copper be introduced into a bottle which is filled with this liquid, and closed so as completely to exclude the air, a portion of the metal equal to that already in solution is dissolved, the metal deriving oxygen from the oxide already in solution, both portions being thus reduced to the state of suboxide; $Cu + CuO = Cu_2O$; the colour gradually disappears, since the suboxide produces a colourless solution with ammonia; but the moment that air is admitted, the blue colour is reproduced. Black oxide of copper is soluble in

oils and fats, so that greasy matters boiled in a copper saucepan, which is not kept bright, are liable to become impregnated with the metal. Oxide of copper combines with glass, and gives it a beautiful green colour. The oxide is hygroscopic, particularly if in a finely divided state, and it absorbs water rapidly from the air. Its oxygen cannot be expelled from it by mere exposure to heat, but if the oxide be plunged into an atmosphere of hydrogen while warm, it is decomposed with evolution of light and heat, while water is formed. Black oxide of copper is soluble in most of the acids, and combines with them to form salts which have a green or a blue colour. When fused with hydrate of potash or of soda, the oxide of copper combines with the alkali, forming a greenish blue mass, which is decomposed by the addition of water.

Thénard obtained a combination of binoxide of hydrogen with oxide of copper; it was of a yellowish-brown colour, and when moist quickly underwent decomposition at ordinary temperatures.

(740) HYDRIDE OF COPPER (Cu_2H).—This substance was obtained by Wurtz, as a brown hydrate, when hypophosphorous acid was mixed with a solution of sulphate of copper, and heated to nearly 140°. It is very unstable: when dry, it is suddenly resolved at 158° F., into hydrogen gas and finely divided metallic copper. It takes fire spontaneously in gaseous chlorine. Hydrochloric acid forms with it subchloride of copper, attended with a brisk disengagement of hydrogen. This disengagement of hydrogen gas is remarkable; Brodie explains it by supposing that the hydrogen of the hydride and that in the acid are in opposite electrical or polar conditions, in consequence of which they unite at the moment of liberation and form *hydride of hydrogen*, or hydrogen gas; thus $Cu_2H + HCl = Cu_2Cl + HH$.

(740 *a*) *Nitride of Copper* (Cu_6N) is obtained by transmitting a current of dry ammoniacal gas over finely powdered oxide of copper heated to 480°; water and nitrogen gas are evolved, and the nitride is left as a dark green powder, which when heated to about 590° explodes feebly, emitting a red light; strong acids decompose it with evolution of nitrogen gas.

(741) SULPHIDES OF COPPER.—These are three in number: Cu_2S; CuS; and CuS_5.

The *Subsulphide* ($Cu_2S = 79{\cdot}5$; *Sp. Gr.* 5·0) is a soft mineral of a dark grey colour, occasionally found native in masses, but sometimes in six-sided prisms. It is easily fused by heat in closed vessels; nitric acid and aqua regia decompose it readily, but hydrochloric acid does not dissolve it. It may be formed by melting together 3 parts of sulphur and 8 of copper; vivid incan-

descence occurs at the moment of combination. It forms the *fine metal* of the copper smelter.

The *Sulphide* ($CuS=47\cdot7$) may be procured by the direct union of its constituents; it is also occasionally found native (*sp. gr.* 3·85) in flexible plates of a blue colour. It may likewise be obtained in the form of a dark brown hydrate, by decomposing any of the salts of copper by a stream of sulphuretted hydrogen; this hydrate is quickly oxidized by exposure to the air, becoming converted into sulphate of copper, and it is dissolved easily by nitric acid and by aqua regia. Sulphide of copper is insoluble in a solution of sulphide of potassium, but it is slightly soluble in one of bisulphide of ammonium.

The *copper pyrites* (*sp. gr.* 4·3) or ordinary ore of copper, consists of a double sulphide of copper and iron, Cu_2S,Fe_2S_3. It is of a yellow colour, and has a brassy lustre: it is sometimes found crystallized in tetrahedra, but it usually occurs in amorphous masses, with a conchoidal granular fracture, and is less hard than iron pyrites. The variety, called variegated or *peacock ore*, contains a larger proportion of sulphide of copper. These compounds are rapidly oxidized and dissolved by nitric acid or by aqua regia, but not by hydrochloric acid.

All the sulphides of copper are decomposed by roasting them in air; if the temperature be high, sulphurous acid escapes, and oxide of copper remains behind; at a lower temperature, sulphate of copper is formed.

Sulphide of copper forms likewise a natural combination with sulphides of lead, silver, antimony, and arsenic, constituting grey copper ore, or *Fahlerz:* this mineral is essentially a quadribasic sulphantimonite and sulpharsenite of copper and iron; it varies considerably in the relative proportions of its constituents, and often contains zinc, lead, silver, and mercury. It crystallizes in forms derived from the regular tetrahedron, and in composition it corresponds to the general formula ($4\,MS,NS_3+4\,M_2S,NS_3$) in which M represents the electro-positive metals, M_2S being usually disulphide of copper or disulphide of silver: whilst N indicates the electro-negative metals, arsenic or antimony. The principal varieties of the ore are:—1. *Tennantite* ($FeS, 3\,CuS,AsS_3+4\,Cu_2S,AsS_3$; *sp. gr.* 4·375), a sulpharsenite of copper and iron, of a leaden-grey colour; the copper in this ore amounts to about 48 per cent. 2. *Light Grey Copper Ore* (*sp. gr.* 4·5 to 4·7), a mixture of sulpharsenite and sulphantimonite of zinc, iron, copper, and silver: colour, steel-grey. 3. *Dark Grey Copper Ore;* (*sp. gr.* 4·7 to 4·9) contains little or no arsenic; it is of an iron black

colour. This variety, and the one preceding it, contain from 35 to 40 per cent. of copper. 4. *Silver Fahlerz* (*sp. gr.* about 5·0), is a dark grey copper ore, rich in silver. The silver varies in this ore from 13 to 30 per cent., and the copper from 14 to 25 per cent.

The *pentasulphide of copper* (CuS_5) was obtained by Berzelius in the form of a blackish brown precipitate, by decomposing a salt of copper with a pentasulphide of one of the metals of the alkalies. It undergoes no change by washing when exposed to the air, but is completely soluble in a solution of carbonate of potash.

A native *selenide of copper* is found in combination with selenide of silver. It occurs in masses of a leaden grey colour, and is very rare, having, hitherto, been found only in Sweden : selenide of copper may be formed artificially by precipitating the sulphate of copper by seleniuretted hydrogen.

Phosphide of Copper (Cu_3P?).—This compound is easily obtained by boiling phosphorus in a solution of sulphate of copper; the liquid speedily becomes decolorized, and a black phosphide of copper, with a semimetallic lustre is formed. It is not soluble in hydrochloric acid, but if thrown into a solution of cyanide of potassium is rapidly decomposed without the application of heat, bubbles of self-lighting phosphuretted hydrogen being disengaged. Abel prepares phosphide of copper by transmitting the vapour of phosphorus over finely divided copper heated in a tube; he finds that this phosphide when mixed with chlorate of potash and gunpowder furnishes a powder of sufficient conducting power for electricity, and at the same time possessed of the requisite inflammability to enable it to be employed with great advantage as a detonating fuse for firing ordnance by magneto-electric currents.

(742) Chlorides of Copper.—Copper forms two chlorides, Cu_2Cl, and $CuCl$.

The *subchloride* ($Cu_2Cl=99$, *Sp. Gr.* 3·376,) is obtained by distilling copper filings with twice their weight of corrosive sublimate; or by dissolving 4 parts of finely divided copper and 5 of the black oxide in hydrochloric acid; or by boiling the chloride with sugar; or by digesting the chloride in closed vessels with metallic copper: the last is a slow process, but part of the subchloride is then deposited in transparent tetrahedra. Subchloride of copper is a white compound, which fuses easily into a yellowish mass. It is insoluble in water, but soluble to some extent in strong hydrochloric acid, with which it forms a pale brown solution, which deposits most of the subchloride on dilution. The solution of the subchloride in hydrochloric acid absorbs carbonic oxide gas with facility: a compound crystallizing in pearly scales (4 Cu_2Cl,

$3\ CO + 7\ HO$? ; Berthelot) may thus be obtained; it is insoluble in water, which however decomposes it, setting subchloride of copper at liberty: it is also quickly decomposed by exposure to the air. Subchloride of copper is soluble in a boiling solution of chloride of potassium; and if the liquid be allowed to cool excluded from the air, octohedral crystals, composed of ($2\ KCl, Cu_2Cl$), are deposited. When the solution in hydrochloric acid is exposed to the air, it absorbs oxygen rapidly, and a pale bluish-green insoluble oxychloride of copper ($CuCl, 3\ CuO + 4\ Aq$) is deposited. This oxychloride is used in the arts as a pigment, under the name of *Brunswick green.* It is best procured by exposing copper clippings to the action of hydrochloric acid, or to a solution of sal-ammoniac in the open air. It occurs native in the form of a green sand, composed of small rhombic prisms, which is found at Atacama in Peru; it has hence been called *Atacamite.* Sometimes it is also found massive. Other oxychlorides of copper of less importance may also be formed. When finely divided copper is boiled in a solution of sal-ammoniac, ammoniacal gas is expelled, and a salt is formed which is gradually deposited in white rhombic dodecahedra, $H_3CuN, CuCl$; it may be regarded as subchloride of copper in which the second equivalent of copper has been displaced by *cuprammonium* (H_3CuN). A solution of this salt when exposed to the air deposits blue crystals consisting of ($H_3CuN, CuCl + H_3CuN, Cl + HO$), and the mother-liquor on further exposure yields cubic crystals of the salt ($H_3CuN, Cl + H_4N, Cl$).

(743) The *Chloride* ($CuCl, = 67{\cdot}2$; *Sp. Gr.* 3·054) may be obtained by the spontaneous combustion of copper in chlorine, but it is more advantageously prepared by dissolving the oxide or the carbonate in hydrochloric acid, when on evaporation it crystallizes in green needles, with the formula ($CuCl + 2\ Aq$) of *sp. gr.* 2·534. A concentrated solution of chloride of copper is of a green colour, but it becomes blue on dilution, and when the salt is anhydrous it is liver-coloured. When heated it fuses, and at a red heat half its chlorine is expelled, and the subchloride remains. It forms double chlorides with the chlorides of potassium and ammonium. The chloride is deliquescent, and very soluble in alcohol. This solution burns with a splendid green flame.

A *double chloride of copper and ammonium* ($H_4NCl, CuCl + 2\ HO$) is obtained in blue square-based octohedra by mixing hot concentrated solutions of the two salts in the proportion of one equivalent of each. Another double chloride ($H_4NCl + 2\ CuCl + 4\ HO$) is obtained in fine, bluish-green crystals, by evaporating a solution of 1 equivalent of sal ammoniac, and 2 equivalents of chloride of copper.

Anhydrous chloride of copper absorbs ammonia rapidly and forms a blue powder ($CuCl, 3\ H_3N$; Rose), which by a heat of 300° loses 2 equivalents of ammonia, and becomes green ($CuCl, H_3N$; Kane). Graham and Kane regard this latter compound as chloride of ammonium, in which the fourth equivalent of hydrogen has its place occupied by copper; hence Graham terms it *chloride of cuprammonium* (CuH_3N,Cl). If ammoniacal gas be transmitted through a hot concentrated solution of chloride of copper, till the precipitate at first formed is redissolved, the liquid on cooling deposits small dark-blue, square prisms, and octohedra, ($H_3CuN, Cl + H_3N,HO$).

It appears therefore that the following well-defined compounds may be obtained by the reaction of the chlorides of copper upon ammonia or muriate of ammonia:—

(1.) $\left.\begin{matrix} H_3CuN \\ Cu \end{matrix}\right\} Cl$

(2.) $\left.\begin{matrix} H_3CuN \\ Cu \end{matrix}\right\} Cl + H_3CuN,Cl + HO$

(3.) $H_3CuN,Cl + 2\ H_3N$

(4.) $H_3CuN,Cl + H_3N,HO$

(5.) H_3CuN,Cl

(6.) $H_3CuN,Cl + H_4N,Cl$

(7.) $H_4N,Cl + CuCl + 2\ HO$

(8.) $H_4N,Cl + 2\ CuCl + 4\ HO$

The *sub-bromide* of copper (Cu_2Br) is insoluble in water.

(744) The *subiodide* of copper ($Cu_2I + Aq$), is a white insoluble powder, which becomes yellow when heated. It is formed by pouring a mixture of 1 equivalent of protosulphate of iron and 1 of sulphate of copper into a solution of any iodide; thus $2\ (CuO, SO_3) + 2\ (FeO,SO_3) + KI = KO,SO_3 + Fe_2O_3, 3\ SO_3 + Cu_2I$. Sulphite of soda may be substituted for the sulphate of iron in this experiment. It has been proposed to employ such a mixture of the two sulphates of iron and copper as a test for determining the quantity of iodine in kelp, in order to fix its commercial value.

SULPHATES OF COPPER.—Copper forms a normal sulphate, and several subsulphates.

(745) *Sulphate of Copper, Blue Vitriol* ($CuO,SO_3 + 5\ Aq = 79{\cdot}7 + 45$) *Sp. Gr. anhydrous*, 3·631, *crystallized*, 2·19.—This salt is manufactured on a large scale, by boiling copper in an iron pot with sulphuric acid, diluted with half its bulk of water: the acid is decomposed and the copper is oxidized at its expense whilst the salt is precipitated. It may also be formed from an artificial sul-

phide of copper, by roasting it with free access of air, and lixiviating the roasted mass to dissolve the sulphate thus produced: the heat must be moderate, or else the sulphate would be decomposed during the roasting. If copper pyrites be used instead of the artificial sulphide, the salt will contain a large quantity of sulphate of iron, which cannot be separated by crystallization; for although the sulphate of copper does not crystallize alone with more than 5 Aq, yet when mixed with sulphate of iron, it, like this salt, assumes 7 Aq and then is isomorphous with the ferrous salt. The only plan in such a case is feebly to ignite the mixed sulphates: the iron parts with its acid at a lower temperature than the copper, and by a second solution the iron is separated in the form of an insoluble oxide. Sulphate of copper is also obtained in considerable quantity as a secondary product in the refining of silver (803): the silver is precipitated from the solution of its sulphate in the metallic form, by plates of copper, and a pure sulphate of copper is thus furnished. 100 parts of the crystals with 5 Aq. contain 31·85 of oxide of copper, 32·07 of sulphuric acid, and 36·c8 of water.

Large quantities of the sulphate of copper are used in calico printing, and it is the salt from which most of the pigments of copper are formed. It is soluble in four times its weight of water at 60°, and crystallizes in beautiful blue crystals of the doubly oblique rhombic form. The powdered crystals absorb hydrochloric acid gas rapidly with evolution of heat, and furnish a deliquescent mass. When sulphate of copper is heated to 212° it loses 4 Aq, and by a temperature of 400° the salt is rendered anhydrous; it then assumes the appearance of a white powder, which becomes blue on the addition of water. The act of combination with water is attended with a hissing noise, owing to the great rise of temperature which attends the action; a considerable evolution of heat also attends the combination of the compound CuO,SO_3,HO, with water. Sulphate of copper is insoluble in alcohol. When heated to bright redness the acid is expelled, and black oxide of copper is left.

Sulphate of copper forms double sulphates both with potash and with ammonia; they are easily obtained by mixing solutions of the salts in equivalent proportions, and allowing them to crystallize. The potash salt is composed of (CuO,SO_3+KO,SO_3+6 Aq; *sp. gr.* 2·244); the ammonia salt of (CuO,SO_3+H_4NO,SO_3+6 Aq; *sp. gr.* 1·891). According to Graham a hot saturated solution of double sulphate of copper and potash deposits a double salt, the composition of which is represented by the remarkable formula [$KO,SO_3+3\,(CuO,SO_3)+CuO,4\,HO$].

Subsulphates.—If a solution of 1 equivalent of sulphate of

copper is boiled with less than 1 equivalent of hydrated oxide of copper, a green insoluble *trisulphate* ($3\ CuO,SO_3+2\ Aq$) is formed. *Brochantite* is a native subsulphate of the metal, composed of ($4\ CuO,SO_3+4\ Aq$); and Denham Smith obtained a subsulphate consisting of ($5\ CuO,SO_3+6\ Aq$).

Anhydrous sulphate of copper absorbs dry ammoniacal gas; the compound consists of [$2\ (CuO,SO_3)+5\ H_3N$; H. Rose]. If ammonia be added in excess to a solution of sulphate of copper, the liquid on evaporation yields dark blue crystals, (CuO,SO_3, $2\ H_3N,HO$; Berzelius); the salt, when heated to 300°, becomes green, losing one equivalent of ammonia and one of water.

(746) *Nitrate of Copper* ($CuO,NO_5+6\ Aq$), is easily made by dissolving copper in nitric acid: it forms a beautiful blue deliquescent salt, which crystallizes in rhomboidal prisms. At temperatures above 60° it crystallizes with 3 Aq in deliquescent needles of *sp. gr.* 2·047. It is very soluble in alcohol; by heat it is decomposed, first into a green *subnitrate* [$CuO,NO_5, 3\ (CuO,HO)$; Gerhardt; *sp. gr.* 2·765], which is insoluble; and if the heat be increased, it is converted wholly into the black oxide of copper, the whole of the acid being expelled. It is this subnitrate which is formed when oxide of copper is heated with monohydrated nitric acid, although the acid may be in considerable excess. If a few crystals of nitrate of copper are moistened and wrapped up in tinfoil they act violently upon the metal and convert it rapidly into peroxide of tin with emission of sparks.

Several basic *phosphates* of copper are found native in small quantities.

(747) CARBONATES OF COPPER.—All attempts to procure the neutral carbonate of copper have hitherto failed. A *hydrated oxycarbonate*, called *Chessylite* [$CuO,HO+2\ (CuO,CO_2)$; *sp. gr.* 3·8], forms a beautiful blue mineral, which crystallizes in oblique rhombic prisms. But the most abundant of the carbonates of copper is the hydrated dicarbonate, or *malachite* ($CuO,HO+CuO,CO_2$; *sp. gr.* 3·7 to 4·0). It forms a very hard mineral of a silky lustre, and a beautiful green colour; it is susceptible of a high polish, by which its concentric and often beautifully veined structure is advantageously displayed. It is often employed for ornamental purposes. Malachite is occasionally found in oblique prisms. Both the blue and the green carbonate are abundant in the copper ore furnished from Australia. A green precipitate, sometimes used as a pigment, which has the same composition as malachite, and is known as *mineral green*, may be obtained by mixing hot solutions of sulphate or nitrate of copper and carbonate of soda. If the solutions

be mixed cold, a pale blue voluminous precipitate is formed, which, according to Brunner, is the same compound, with an additional equivalent of water ($CuO,HO + CuO,CO_2 + HO$). By boiling the precipitated carbonate, it becomes first green and then black, losing nearly all its water and carbonic acid. A double carbonate of potash and copper ($KO,CO_2 + 5\,CuO, 4\,CO_2 + 10\,Aq$) may be obtained by digesting the green carbonate in a solution of bicarbonate of potash: it is deposited in blue crystals by spontaneous evaporation. Similar salts may also be formed with soda and ammonia.

(748) CHARACTERS OF THE SALTS OF COPPER.—1. *Salts of the Dioxide,* or *Cupreous Salts.*—Nearly all of them are insoluble in water, but soluble in hydrochloric acid; in this form they absorb oxygen rapidly, and are converted into salts of the black oxide. They are unimportant, and have been but little studied; one of their most remarkable properties is their power when in solution in hydrochloric acid of absorbing carbonic oxide, with which they form a crystalline compound.

2. *Salts of the Black Oxide,* or *Cupric Salts.*—Most of these salts of copper have a green or a blue colour when hydrated, but they are white when anhydrous; they are almost all soluble. They have a strong, disagreeable metallic taste, and act as poisons to the animal frame, producing violent and irrepressible vomiting and purging, followed by exhaustion and death. They form an insoluble compound with albumen, which is nearly inert; raw whites of eggs should therefore be administered in cases of poisoning suspected to be occasioned by this metal. Milk or sugar mixed with iron filings, by reducing the salts of the black oxide of copper to salts of the suboxide, or to the metallic state, are also valuable adjuncts.

The salts of the black oxide of copper are easily recognised when in solution: though neutral in composition they redden litmus. *Potash and soda* give in their solutions a pale blue voluminous precipitate of hydrated subsalt; an excess of the alkali does not dissolve it, but converts it into a blue hydrated oxide, which becomes black and anhydrous when the liquid is boiled with it. If sugar or tartaric acid, or certain other organic substances be present, the blue precipitate is redissolved by an excess of the alkaline liquid, and forms a blue solution. *Ammonia* gives a similar blue precipitate, but an excess of the alkali redissolves it, forming a deep blue solution, which is very characteristic. *The carbonates of potash and soda* give a pale blue hydrated basic carbonate, which becomes converted into the black oxide when

boiled in the liquid. *Carbonate of ammonia* also gives a blue precipitate, but redissolves it if added in excess, forming an intensely blue solution. *Ferrocyanide of potassium* yields a bulky brown precipitate, insoluble in hydrochloric acid but soluble in ammonia, which leaves it unaltered on evaporation. *Sulphuretted hydrogen* gives even in acid solutions a brownish-black hydrated sulphide. The last two characters distinguish the salts of copper from those of nickel, which also form a blue solution with ammonia. Sulphide of copper is almost insoluble in ammonia, and in hydrosulphate of ammonia, but is dissolved by cyanide of potassium. Another characteristic and very delicate test of the presence of copper is afforded by the action of a polished plate of *iron*, which, in a feebly acid solution, is speedily covered with a red deposit of metallic copper. *Zinc* precipitates copper in the form of a black powder, which assumes a metallic lustre under the burnisher. If a salt of copper be heated with soda on charcoal *before the blowpipe* in the reducing flame, a bead of metallic copper may be obtained, and may be recognised by its colour and its malleability. Most copper salts when heated on platinum wire communicate an intense green colour to the oxidizing flame.

In cases in which the presence of copper is suspected in admixture with organic matters, as in the contents of the stomach, where it is supposed to have acted as a poison, the material must be reduced to dryness, and incinerated in an earthen crucible. The ash is then to be treated with nitric acid, and the liquid tested with ammonia, with ferrocyanide of potassium, and with a steel needle. The copper-coloured deposit on the steel may be further identified by placing it in a narrow tube with a few drops of ammonia, which will become blue in the course of 24 hours if copper be present (Taylor).

The salts of copper have considerable tendency to form double compounds with other salts, and frequently subsalts of this metal may be procured with various acids: those with the sulphuric, nitric, carbonic, and acetic acids, are the most important.

(749) *Estimation of Copper.*—This is generally effected in the form of the black oxide, 100 parts of which correspond to 79·82 of the metal. If the solution contain no metal precipitable by potash, an excess of potash is added, and the liquid is boiled; the precipitate is well washed with boiling water.

Pelouze (*Ann. de Chimie*, III. xvi. 426) has described a method of estimating the quantity of copper, by bringing it into solution with excess of ammonia, and ascertaining the quantity of a standard solution of sulphide of sodium which is required to decolorize the

liquid. The process is rapid, and admits of being applied in a large number of cases.

A still better method, according to E. O. Brown (*Q. J. Chem. Soc.*, x. 65), consists in treating the solution of copper with one of iodide of potassium; subiodide of copper (Cu_2I) is thus formed, and iodine is set at liberty: the amount of the latter is determined by a standard solution of hyposulphite of soda: in order to effect the operation a weighed quantity of the ore is dissolved in nitric acid, boiled till red fumes cease to escape, and the nitrous acid is all expelled; it is then diluted with water, and carbonate of soda added until a slight permanent precipitate is formed. Acetic acid in excess is added, and afterwards an excess of iodide of potassium and a few drops of a solution of starch. The quantity of iodine thus set free is then estimated by the number of divisions of a standard solution of hyposulphite of soda required to oxidize the iodine, a point which admits of most accurate determination by the disappearance of the blue tinge. The solution of hyposulphite is graduated by dissolving 5 grains of pure copper in nitric acid, and subjecting it to a series of operations exactly corresponding to those performed upon the ore, noting the number of divisions of the standard solution consumed in oxidizing the amount of iodine set free.

Copper may be readily separated from the metals of the first four groups, with the exception of cadmium, by the action of sulphuretted hydrogen. The precipitated sulphide of copper must be washed with water containing sulphuretted hydrogen in solution, in order to prevent its oxidation on the filter. The precipitate must be detached from the filter, redissolved in nitric acid (610), and the oxide of copper precipitated by means of potash.

If cadmium be present, Stromeyer directs that the precipitate of the mixed sulphides, obtained by transmitting sulphuretted hydrogen through the liquid, be redissolved by nitric acid, and precipitated by an excess of carbonate of ammonia, which, if left to stand for a few hours, dissolves the copper, but leaves the cadmium in the form of carbonate.

The separation of copper from bismuth may be effected by means of carbonate of ammonia, as directed for cadmium.

The other metals of the fifth group are separated by precipitating them with the copper as sulphides, and then digesting the mixed sulphides with a solution of sulphide of potassium (sulphide of ammonium dissolves traces of copper); the sulphide of copper alone remains undissolved.

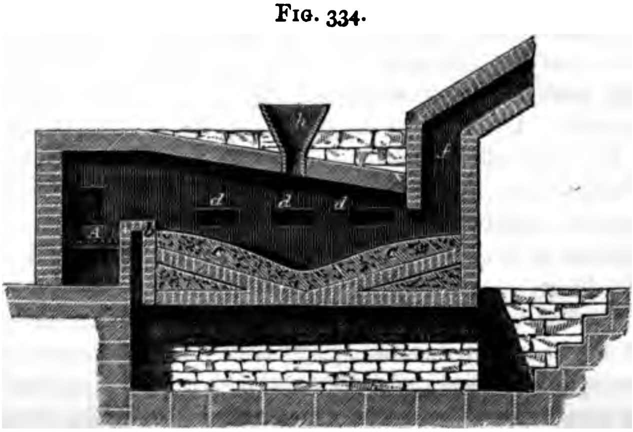
§ II. Lead ($Pb=103{\cdot}6$). *Sp. Gr.* 11·36.

(750) Almost all the lead of commerce is obtained from galena, the native sulphide of lead. It occurs, mixed with quartz, blende, pyrites, sulphate of baryta, and fluor-spar, in veins traversing the primitive rocks, and particularly in the clay-slate in Cornwall, and mountain limestone in Cumberland. Small quantities of carbonate and phosphate of lead are frequently met with, but they are unimportant as ores of the metal. Galena always contains a small proportion of sulphide of silver; when the mineral is found in bold, well-characterized cubes, it is usually nearly pure. The proportion of silver in galena is liable to considerable variation; a mineral yielding 120 ounces of silver to the ton, or 0·36 per cent., is considered to be extremely rich. England and Spain afford the principal supply of this metal, about 65,000 tons of lead being annually raised in England, which furnish on the average 560,000 ounces of silver.

(751) *Extraction.*—After the lead ore has been raised to the surface, it undergoes a careful mechanical preparation, conducted upon the principles already explained (436); and having been thus freed to a great extent from its earthy impurities, it is ready for smelting.

If the galena be tolerably free from siliceous gangue, this operation is sufficiently simple. About $1\frac{1}{4}$ ton of the dressed ore is mixed with from $\frac{1}{40}$ to $\frac{1}{20}$ of its weight of lime, and is heated to dull redness in a reverberatory furnace, through which a strong current of air is passing. Fig. 334 exhibits a section of the reducing

Fig. 334.



furnace employed in Derbyshire. *A* is the fire grate, *b* the

bridge, *h* the hopper by which the charge is introduced; *c c*, the bed on which the ore is placed, sloping downwards towards a gutter in the centre by which the melted metal is drawn off; *d, d, d,* are doors for working the charge and for admitting air, the draught of the furnace being completely under control by a damper placed in the flue *f*.

During the roasting a large quantity of the sulphur burns off as sulphurous acid, and a portion of oxide of lead is formed: another portion of the sulphide of lead is converted into sulphate of lead, and much of the ore still remains undecomposed. In the course of the operation, the mass is frequently stirred, and care is taken not to allow the temperature to rise sufficiently high to fuse it. When it is considered that the roasting has been carried far enough, the materials in the bed of the furnace are thoroughly mixed together, the furnace doors are closed, and the heat is suddenly raised. The oxide and the sulphate of lead then react upon the undecomposed sulphide of the metal; a large quantity of sulphurous acid is evolved, whilst metallic lead runs copiously from the mass. The successive stages of this operation may be traced as follows:—

One equivalent of sulphide of lead, by combining with 3 equivalents of oxygen, furnishes 1 equivalent of oxide of lead and 1 of sulphurous acid, as is exhibited by the equation: $PbS + 3O = PbO + SO_2$. If the equivalent of galena unite with 4 equivalents of oxygen, 1 equivalent of sulphate of lead is formed: $PbS + 4O = PbO,SO_3$. Both oxide of lead and sulphate of lead, when heated with fresh sulphide of lead, are decomposed, metallic lead and sulphurous acid being in each case the result of the reaction. Two equivalents of oxide of lead and 1 of galena furnish 3 of lead and 1 of sulphurous acid: $2PbO + PbS = 3\,Pb + SO_2$. One equivalent of sulphate of lead, when heated with 1 of galena, yields 2 equivalents of lead and 2 of sulphurous acid: thus $PbS + PbO,SO_3 = 2Pb + 2SO_2$. During the roasting a portion of subsulphide of lead, Pb_2S, is also produced. This substance forms a fusible matt, which flows from the furnace with the metallic lead, constituting a stratum which floats above the melted metal. This subsulphide of lead is again returned to the furnace and roasted with fresh ore.

After the melted mass has been drawn off into cast-iron basins placed for its reception, a few spadefuls of lime to which a quantity of fluor-spar is sometimes added, are thrown into the furnace, with a view to act upon the scoriæ which remain behind in considerable quantity: the lime decomposes the fusible silicate of lead, liberates

oxide of lead and forms a less fusible silicate of lime, and the fluor-spar forms a fusible compound with the sulphate of lime, or sulphate of baryta, if either of them is present. The scoriæ usually contain an excess of oxide and sulphate of lead; they are therefore mixed with coke or charcoal, and exposed to heat on the bed of the furnace, after the doors have been carefully closed; the oxide of lead then becomes reduced by the carbon.

Refining of Lead.—Lead which contains antimony or tin is harder than the pure metal, and is subjected to a further operation, termed *improving*, in order to refine it. This consists simply in melting the lead, and heating it for a period, longer or shorter, as may be necessary, in a shallow cast-iron pan set in the bed of a reverberatory furnace; the antimony and tin being more oxidizable than the lead, are thus removed in the pellicle of oxide which is continually forming. From time to time the workman takes out a small sample of the metal to examine the appearance which it presents on cooling. As soon as it exhibits a peculiar flaky crystalline appearance on the surface, the oxidation has been carried far enough, and the metal is then run off and cast into pigs.

(752) *Concentration of Silver in Lead by Pattinson's process.*—Silver may be profitably extracted from lead, even when the quantity does not exceed from three to four ounces of silver to the ton, by a process introduced by Mr. Pattinson, of Newcastle. This gentleman observed that if melted argentiferous lead be briskly stirred during slow cooling, a portion of the metal solidifies first, in the form of crystalline grains, which sink to the bottom of the portion which remains melted. These crystals consist of lead nearly free from silver; the fusing point of the argentiferous alloy occurring at a lower temperature than that of pure lead. This observation is turned to account in the following simple manner:—

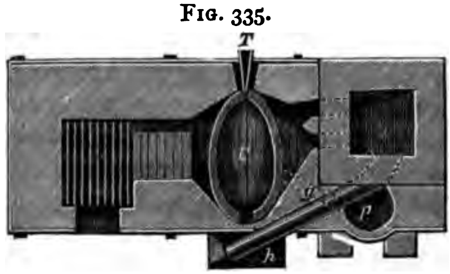
Eight or nine cast-iron pots, each capable of containing about five tons of melted lead, are arranged in a row, set in brickwork, and each provided with a separate fireplace underneath. A quantity of lead is introduced into the middle pot, and melted; the fire is then withdrawn, and the metal is briskly stirred by the workman whilst it cools: the crystals of lead subside as they form, and are removed at intervals by means of a large perforated iron ladle, and transferred to the next pot on the right hand. When about four fifths of the metal have been thus removed in grains, the concentrated argentiferous alloy is ladled out into the next pot on the left-hand side, and the empty pot is charged with a fresh portion of lead, which is subjected to a similar treatment. When the pot

to the right and to the left has in this manner received a sufficient quantity either of poor or of argentiferous lead, it is subjected to a similar operation; the concentrated argentiferous portion being passed off continually to the next pot on the left, whilst the crystalline or poorer portion is handed over to the next pot on the right-hand side. The last pot to the left thus at length becomes filled with lead which may contain 300 ounces of silver to the ton; it is not found advantageous to concentrate it beyond this point: the lead which accumulates in the last pot on the right-hand side does not contain more than half an ounce of silver in the ton. This poor lead is much improved in quality by the operations which it has undergone, and is at once cast into pigs for the market.

(753) *Extraction of Silver from Lead by Cupellation.*—The rich argentiferous lead is now subjected to *cupellation*. This process is founded upon the circumstance that lead, if exposed at a high temperature to a current of air, rapidly absorbs oxygen, and is converted into a fusible oxide, whilst silver does not become oxidized, but is left behind in the metallic state. The litharge or oxide of lead melts at a high temperature, and flows off the convex surface of the melted metal, and thus continually exposes a fresh surface of lead to the action of the air.

In England the cupellation is performed in a low-crowned reverberatory furnace, the hearth of which is moveable. This hearth or *cupel* is shewn in the plan of the furnace (Fig. 335); it consists of a shallow oval basin, C, composed of a mixture of bone ash with fern or wood ashes; this mixture is slightly moistened, and beaten into an iron ring about 4 feet in its long diameter, and 2 feet in the shorter: the cupel is introduced into the furnace from beneath, and is supported by bricks, so that it can be readily removed and renewed,—an operation which is generally required once a week. When dry, the fire is cautiously lighted and the lead introduced; a continual blast of air from a tuyère, T, is made to play over the surface of the melted metal; litharge is formed abundantly, and runs off through a gutter, *g*, for the purpose, into an iron pot, *p*, placed beneath the furnace for its reception; in front is a hood, *h*, for carrying off the fumes of oxide of lead which would otherwise escape and injure the workmen. Fresh

FIG. 335.



lead is added from time to time to supply the place of that which is oxidized; until at length a quantity of lead, originally amounting to about 5 tons, is reduced to between 2 and 3 cwt. This melted metal is withdrawn by making a hole through the bottom of the cupel; the aperture is afterwards closed with fresh bone ash, and another charge is proceeded with. When a quantity of rich lead sufficient to yield from 3000 to 5000 ounces of silver, has thus been obtained, it is again placed in a cupel, and the last portions of lead are removed. It is found advantageous to effect this final purification of the concentrated silver-lead separately, because in the last stages of the operation the litharge carries a good deal of silver down with it: these portions of litharge, therefore, on being reduced, are again subjected to the desilvering process.

The litharge from the first fusion is either sold as oxide of lead, or it is reduced in a small reverberatory furnace with anthracite, or powdered coal. The porous cupels absorb a large quantity of litharge, and they likewise are passed through the furnace in order to extract the metal.

A very beautiful phenomenon, known as the *fulguration* of the metal, attends the removal of the last portions of lead from the silver. During the earlier stages of the process the film of oxide of lead, which is constantly forming over the surface of the melted mass, is renewed as rapidly as it is removed; but when the lead has all been oxidized, the film of litharge upon the silver becomes thinner and thinner as it flows off; it then exhibits a succession of the beautiful iridescent tints of Newton's rings; and at length the film of oxide suddenly disappears, and reveals the brilliant surface of the metallic silver beneath.

In the Hartz the hearth of the cupellation furnace is fixed, and is made of brick, covered with marl, which is renewed after each operation, but the cover of the furnace is moveable. Karsten states that the advantage of this method is, that the litharge runs off more perfectly, and that there is less waste of silver from absorption into the cupel and less expenditure of labour and fuel upon recovering the lead from the bottom of the furnace, which absorbs but comparatively little litharge.

(754) In the North of England, the galena is smelted by a process somewhat different: the ore is first roasted, and then reduced in a small square blast furnace, or forge hearth,—dried peat being the fuel principally employed. This form of furnace is known as the *Scotch furnace*.

In some parts of the Hartz, where the ores are largely mixed with siliceous matters, the English method of smelting is not ap-

plicable, as the silica combines with the oxide of lead, and forms a fusible slag. It is found necessary in these cases to reduce the sulphide of lead by means of metallic iron, which is added in the form of granulated cast-iron, in the proportion of about 1 part of iron to 20 of pure galena. The fusion is performed in a small blast furnace, about 20 feet high, and 3 feet across at the widest part.

These various furnace operations are attended by a continual disengagement of white fumes, which consist principally of oxide and sulphate of lead, and are technically termed *froth of lead;* in this way nearly a seventh of the whole lead is volatilized. Independently of the waste thus occasioned, the fumes are highly deleterious; it is therefore of great importance to prevent as far as possible their diffusion through the air. It is stated, that in the Hartz about $\frac{7}{10}$ of the volatilized portion is arrested by causing the gases from the furnaces to pass through a succession of condensing chambers, before they finally escape into the air.

(755) *Properties.*—Lead is a bluish-white metal, so soft that it may easily be made to take impressions; it leaves a streak upon paper, and may be cut with the nail. It may be laminated into tolerably thin sheets, as well as drawn into wire; but both in ductility and tenacity it is low in the scale. It fuses at 620° (Person; or 617° Rudberg), and may with some difficulty be obtained in cubic or in octohedral crystals as it cools. Lead contracts considerably at the moment of its solidification, and it is therefore not well adapted for castings. It appears to have the power, when melted, of dissolving a small quantity of oxide of lead, by which the hardness of the metal is much increased; but its softness may be restored by keeping it melted under charcoal for some time, with occasional agitation. As a conductor of heat and electricity, it is inferior to many of the metals.

(756) *Combined Action of Air and Water on Lead.*—The surface of a piece of lead when freshly cut presents a high metallic lustre, but it soon tarnishes by exposure to air, owing to the formation of a thin, closely adhering film of oxide, which protects the metal from further change. Lead undergoes no alteration in a perfectly dry atmosphere, and even when sealed up in a vessel of pure water, which has been boiled for some time to expel the air, the metal will retain its brilliancy for an indefinite period; but if it be exposed to the united action of air and *pure* water, it is subject to a powerful corrosion. As the result of this exposure the lead becomes oxidated at the surface, and the water dissolves the oxide of lead; this solution absorbs carbonic acid, a film of hydrated oxycarbonate of lead ($PbO,HO+PbO,CO_2$) is deposited

in silky scales, and a fresh portion of oxide is formed and dissolved by the water; thus a rapid corrosion of the metal takes place. This action is modified very materially by the presence of various salts in the water, even though the quantity of these salts may not exceed 3 or 4 grains in the gallon. The corrosion is much increased by the chlorides and nitrates. The presence of very minute quantities of the nitrites in water confers upon it a corrosive action on lead. Both nitrites and nitrates are often present in spring and river waters, owing to the decomposition of organic matter, and it is not improbable that the unexplained corrosive action of certain soft waters upon lead may be due to the presence of these salts, which might easily be overlooked in the course of the analysis (Medlock). Small quantities of ammonia also favour the solution of the metal. On the other hand, the corrosion is diminished by the sulphates, the phosphates, and the carbonates. Oxide of lead, indeed, is scarcely soluble in water which contains these salts in solution. Bicarbonate of lime is especially remarkable for the preservative influence which it exerts, and as this latter is a very usual impurity in water, few spring waters act on the metal to any dangerous extent. In these cases a film of insoluble carbonate of lead is formed upon the surface, and the metal beneath is protected from further injury. The action of water on lead is a matter of great importance in its sanitary bearings, on account of the extensive employment of this metal in cisterns and pipes for the storage and supply of water. Rain water as collected from the roofs of houses, is for the most part sufficiently impure, especially in large towns, to prevent its action upon the metal. Of all the salts of lead the hydrated oxycarbonate is the least soluble, pure water not taking up more than 1 part in 4 millions, or about $\frac{1}{60}$th of a grain per gallon. If a solution of oxide of lead in distilled water, containing 4 or 5 grains to the gallon, be exposed to the air, it soon becomes filled with silky crystals of the hydrated oxycarbonate, owing to the absorption of carbonic acid; and in a few hours the water does not contain more than $\frac{1}{1000000}$ of the metal in solution. Water highly charged with carbonic acid may nevertheless dissolve lead to a dangerous extent, owing to the solubility of carbonate of lead in excess of carbonic acid; when water thus impregnated with lead is boiled, the gas is expelled, and the carbonate subsides. So general, however, is the action of water upon lead, that it is rare to find any that has been kept in cisterns of this metal perfectly free from all traces of it. Slate cisterns are therefore greatly to be preferred to leaden ones.

At high temperatures, lead absorbs oxygen rapidly from the

air; it undergoes partial volatilization, and emits white fumes of oxide. It is not acted upon by sulphuric or hydrochloric acid at ordinary temperatures, and but slightly even when boiled with them; but it is dissolved with extrication of binoxide of nitrogen by nitric acid, especially when the acid is somewhat diluted. The alkalies do not exercise any decided influence upon it. Chlorine also slowly converts the metal into chloride, but the film of this compound, which is formed on the surface, protects the metal beneath. In the presence of moisture, lead is corroded when in contact with sulphate of lime; hence in its application to architectural purposes, the contact of stucco or plaster with lead should be avoided.

The lead of commerce is often nearly pure. The purest specimens are the softest. Traces of tin, iron, copper, and silver, and sometimes of antimony and manganese, are the impurities which are most often observed. In order to obtain it perfectly pure, it should be reduced with black flux from the oxide left by igniting the pure nitrate or carbonate of the metal.

(757) *Uses.*—From its softness, fusibility, durability, and the ease with which it may be worked, lead is applied to a multiplicity of purposes. The reception chambers in the manufacture of sulphuric acid are lined with it. It forms the ordinary material for cisterns, water-pipes, and gutters, and is frequently employed in covering the roofs of houses. The alloys of lead are numerous and important. Shot for fowling-pieces is an alloy of lead with a small proportion of arsenic, which hardens it and facilitates its granulation into globules; the quantity of arsenic varies with the purity and softness of the lead: usually it requires from 3 to 8 parts in the 1000. The common white arsenic of the shops is added to the lead, melted in a covered vessel; the arsenious acid is reduced by the lead, and the oxide of lead thus formed rises as a film to the surface of the alloy. Sonnenschein observed an alloy of iron and lead ($FePb_2$) which had been accidentally formed in a blast furnace, in acicular feathery crystals; it was yellow, harder than lead, and of sp. gr. 10·36; it contained 11·14 per cent. of iron.

When lead is alloyed with about one fourth of its weight of antimony, it forms *type metal*: this alloy is sufficiently fusible to allow of its being readily cast; it expands at the moment of solidification, and copies the mould accurately; it is hard enough to bear the action of the press, and yet not so hard as to cut the paper. The ordinary *fusible metal* contains lead, as do the various compounds called pewter, Britannia metal, and Queen's metal. The solder used by tinplate workers and plumbers is a mixture of

lead and tin (676). When lead is melted with zinc, a white, hard, ductile alloy is formed. *Pot metal* is an alloy of lead and copper, obtained by throwing lumps of copper into red-hot melted lead (Brande): it is of a grey colour, brittle, and granular.

Other compounds of lead are also largely employed in the arts. The red oxide enters in large proportion into the constitution of flint glass. The carbonates, the oxychlorides, and the chromates are extensively used as pigments.

(758) COMPOUNDS OF LEAD WITH OXYGEN.—Lead forms four oxides;—an unimportant black dioxide, Pb_2O, obtained by heating the oxalate to about 600°, in a glass retort. A protoxide, PbO, which is the basis of the ordinary salts of the metal, consisting in 100 parts of 92·82 of lead and 7·18 of oxygen; a binoxide, PbO_2, which is insoluble in acids, 100 parts of which contain 86·61 of lead and 13·39 of oxygen; and red lead, which is a compound of the two oxides last mentioned, usually in the proportions indicated by the formula ($2PbO,PbO_2$).

Protoxide of Lead (PbO=111·6); *Sp. Gr.* 9·2 to 9·5.—This oxide is well known under the name of *Litharge.* Its colour varies according to the mode of its preparation. Usually it is obtained on a large scale by the oxidation of lead in a current of air, in which case it forms a scaly mass, which, if of a yellow colour, is commonly termed litharge of silver; if redder, it is termed litharge of gold. The former is the purer, as the red colour is due in many cases to the presence of a small quantity of minium. If the oxidation be effected at a temperature below that required for the fusion of the oxide, a yellow powder termed *massicot* is obtained. Common litharge, when reduced to a fine powder, also has a dull yellow colour; when heated, it assumes a brown-red colour, which disappears again as it cools. If a hot solution of caustic soda, of sp. gr. 1·42, be saturated with litharge, the oxide is deposited, as the liquid cools, in beautiful anhydrous rose-coloured crystals. If the solution of oxide of lead in caustic soda be allowed to evaporate spontaneously by exposure to the air, the alkali gradually absorbs carbonic acid, and the oxide is deposited in transparent anhydrous dodecahedral crystals.

If a salt of lead be precipitated by the addition of a caustic alkali, in slight excess, the oxide of lead is precipitated in the form of a white hydrate (2PbO,HO). Another hydrate (3PbO, HO) may be obtained in groups of transparent octohedrons, or of four-sided prisms mixed with anhydrous crystals, by precipitating a solution of triacetate of lead by an excess of ammonia, at a temperature of 86°.

Both litharge and the hydrated oxide of lead absorb carbonic acid slowly from the atmosphere.

Protoxide of lead fuses at a heat above redness, and crystallizes on cooling in semi-transparent scales. When fused, it combines rapidly with the earths and with silica, speedily destroying and penetrating the crucibles in which it is melted. It should not be fused in platinum crucibles, since it becomes decomposed into peroxide, and metallic lead; the latter attacking and spoiling the crucible. The oxide is slightly soluble in water, to which it communicates an alkaline reaction. The presence of a very small quantity of saline matter diminishes or prevents the solution of the oxide; the solution absorbs carbonic acid rapidly from the air, and mere filtration in many cases causes the deposition of a large portion of the oxide in the form of hydrated oxycarbonate.

Oxide of lead is soluble in solutions of the caustic alkalies; indeed it forms compounds with the alkalies and alkaline earths which have been obtained in crystals; they are, however, decomposed by simple exposure to the atmosphere, owing to the absorption of carbonic acid. The solution of the oxide in lime-water is sometimes used as a hair dye: the lime softens and partially decomposes the hair, and the lead of the oxide, combining with the sulphur of the hair, forms sulphide of lead, which stains the hair of a permanent black. Litharge is in continual requisition by the assayer as a flux; it also enters largely into the composition of the glaze of common earthenware. A mixture of 1 part of massicot with 8 or 10 of brick-dust, made into a paste with linseed oil, forms *Dhil mastic*: it sets exceedingly hard and is frequently employed to repair defects in stone facings. The stone should be moistened before applying the mastic.

Oxide of lead is a powerful base. It has a strong tendency to form subsalts; those which it yields with acetic acid, and some of those with nitric acid, are soluble; they exert a strongly alkaline reaction upon test-paper, and absorb carbonic acid with avidity. Indeed, owing to the very sparing solubility of the basic carbonate of lead, a solution of a subsalt of lead is the most delicate test for the presence of carbonic acid, either in a gas or in distilled water; a mere trace of carbonic acid occasions the formation of the peculiar silky crystalline precipitate which characterizes the basic hydrated oxycarbonate of lead.

(759) *Minium*, or *Red Lead* (*sp. gr.* about 9·08), is a compound of protoxide of lead with the peroxide of the metal. It was obtained by Berzelius as PbO,PbO_2, but its most usual composition is represented by the formula $2\,PbO,PbO_2$, though well crystallized

samples have been formed, which consisted of 3 PbO,PbO_2. All these compounds possess a brilliant red colour. If the latter two be treated with a solution of potash, or with one of normal acetate of lead, the excess of oxide of lead may be dissolved out, and the compound PbO,PbO_2 is left.

Red lead is obtained by heating metallic lead, so as first to procure the protoxide or massicot, keeping the temperature below the fusing point of the oxide; the oxide so obtained is finely levigated in water, and the particles which are held in suspension are allowed to subside, dried, and exposed in iron trays, to a heat of about 600°, in a reverberatory furnace. The additional quantity of oxygen is gradually absorbed. If white lead is submitted to a similar roasting, the carbonic acid is expelled, and minium of very fine quality is obtained by the gradual absorption of oxygen. The principal use of red lead is in the manufacture of flint glass. Much care is required in the preparation of minium for this purpose; it is necessary that it should be free from the oxides of other metals, which would impart colour to the glass. In the oxidation of the lead, which constitutes the first stage in the preparation of red lead, the metals which are more oxidizable than lead are removed with the first portions of oxide; whilst the copper and silver accumulate in the portions of oxide which are produced last. The intermediate stage of the operation is therefore that which furnishes the purest oxide. Minium is better suited to the glassmaker than litharge, because the excess of oxygen burns off any combustible matter which may accidentally be present, and converts the protoxide of iron into peroxide. Red lead is also used for colouring the inferior kinds of red sealing wax, and for paper staining.

If minium be exposed to a high temperature it is decomposed, oxygen is evolved, and the protoxide of lead remains. Minium is insoluble in the acids, but by many of them, especially by nitric acid, it is decomposed; a salt of the protoxide is formed, and the brown peroxide of lead remains behind.

(760) *Peroxide of Lead* (PbO_2=119·6; *Sp. Gr.* 9·45).—This compound is occasionally found native in iron-black brilliant hexahedral prisms, forming *heavy lead ore*. It is usually prepared by levigating minium very finely, and digesting the powder in boiling nitric acid, diluted with 4 or 5 times its bulk of water; the residue is washed with fresh nitric acid, and then with water, till everything soluble is removed. It may also be obtained by gently heating a mixture of 4 parts of litharge in fine powder, with 1 part of nitrate of potash, and washing the product with water.

Wöhler prepares the peroxide by transmitting a current of gaseous chlorine through the magma obtained by mixing a solution of 4 parts of acetate of lead with one of 3 parts of crystallized carbonate of soda: the carbonate of lead becomes gradually but completely converted into peroxide of lead, and must be thoroughly washed; chloride of sodium is formed, and acetic and carbonic acids are set free, as follows:—

$$PbO,C_4H_3O_3 + NaO,CO_2 + Cl + HO = PbO_2 + HO,C_4H_3O_3 + NaCl + CO_2.$$

Various other oxidizing agents may be employed to convert the protoxide into the peroxide of lead: thus acetate of lead when heated with a solution of bleaching powder yields the binoxide in crystals.

Peroxide of lead is insoluble in water and in acids; it is converted by heat under disengagement of oxygen into the protoxide; sulphurous acid instantly decomposes it, forming sulphate of the protoxide; $PbO_2 + SO_2 = PbO,SO_3$; hence it is frequently employed in the laboratory to absorb sulphurous acid when mixed with other gases. If digested in a solution of ammonia, or subjected to a current of this gas, mutual decomposition occurs; water, nitrate of ammonia, and protoxide of lead are formed. Cold diluted hydrochloric acid dissolves this oxide, forming a rose-coloured solution, from which the alkalies reprecipitate the peroxide; but if the acid be employed hot, or in a concentrated form, chloride of lead is produced, and chlorine is set free. If the peroxide be mixed with a fifth of its weight of sulphur, the mixture takes fire by friction; sulphurous acid and sulphide of lead being produced.

Peroxide of lead appears to possess the properties of a feeble acid. By fusing the pure peroxide with excess of caustic potash or of soda, in a silver crucible, and dissolving the residue in a small quantity of hot water, crystals of *plumbate* of potash or of soda are formed as the solution cools: plumbate of potash consists of $KO,PbO_2 + 3\ Aq$; (Fremy). Pure water decomposes these compounds, and the peroxide of lead subsides. Like the peroxides of silver and manganese, the peroxide of lead is a conductor of electricity, and is formed at the zincode of the battery when aqueous solutions of the protosalts of lead are decomposed by the voltaic current.

(761) COMPOUNDS OF SULPHUR WITH LEAD.—The most important of these is the protosulphide, PbS, the *galena* of mineralogists. Besides this a subsulphide, Pb_2S, is formed as the *lead matt* in reducing galena; and a red persulphide is also obtainable,

though its composition is not accurately known: it is quickly resolved in the liquid into protosulphide of lead and free sulphur. This persulphide is procured by adding a solution of a persulphide of one of the metals of the alkalies to a solution of a salt of lead.

Protosulphide, or *Galena* ($PbS = 119{\cdot}6$; *Sp. Gr.* 7·59).—Galena is an abundant mineral, and forms the principal ore of lead; it is a brittle substance, and is found crystallized, more or less distinctly, in cubes of a deep leaden colour and strong metallic lustre. It may be formed artificially by fusing lead with sulphur; or it may be precipitated as a hydrate by treating any of its salts, either in solution or in suspension in water, with sulphuretted hydrogen. When heated in closed vessels, part of the sulphur is expelled, and a *subsulphide* (Pb_2S) left; this subsulphide is formed on the large scale in the process for reducing galena; it is, however, decomposed by a moderate heat, as the lead melts out in the metallic form, leaving the protosulphide, which, though fusible, is less so than the metal itself. Galena, when heated in contact with air, is oxidated, part of the sulphur burns off, and a mixture of oxide of lead and sulphate of lead is formed. Nitric acid and aqua regia decompose it, converting it into sulphate: hydrochloric acid acts but slowly upon it in the cold, but at a boiling temperature it decomposes it freely and evolves sulphuretted hydrogen. When this sulphide is fused with lime or with the alkalies, metallic lead is obtained. If heated with oxide of lead or of iron, it is reduced with escape of sulphurous acid. When heated with a small quantity of nitre a similar result is obtained. When the sulphide of lead is heated with metallic iron it is decomposed, sulphide of iron and metallic lead being the result. Advantage is taken of this fact in the assay of galena; 200 grains of the powdered ore are mixed with 300 of black flux, 3 or 4 blacksmith's nails are placed in a Cornish crucible with their heads downwards, the mixture is introduced, and covered with a small quantity of fused and powdered borax. It is heated to full redness for 10 minutes: the nails are withdrawn, and, when cold, the crucible is broken, and the button of metallic lead is weighed.

(762) Chloride of Lead ($PbCl = 139{\cdot}1$) is best prepared by precipitating a solution of nitrate of lead by the addition of a solution of chloride of sodium; a sparingly soluble, white, heavy precipitate occurs. It is soluble in about 33 parts of boiling water, but it is taken up more sparingly if an excess of hydrochloric acid be present; the concentrated acid, however, dissolves it readily. It is easily fusible into a semi-transparent, horny, sectile mass, and at high temperatures may be volatilized. If kept fused in air till

no more fumes arise, it is converted into an oxychloride (PbO,PbCl). The alkalies at first convert it into an oxychloride, and if the action be prolonged, into pure oxide.

Oxychlorides of Lead.—The chloride combines with oxide of lead in several proportions. One of these forms a white, translucent, fusible, colourless mineral (2 PbO,PbCl), which is found in the Mendip Hills crystallized in right rhombic prisms. Mr. Pattinson manufactures a white oxychloride of lead (PbO,PbCl), by acting on powdered galena with hydrochloric acid: the chloride of lead thus obtained is dissolved in hot water, and precipitated by the addition of lime-water in quantity just sufficient to remove half the chlorine; CaO + 2 PbCl = CaCl + PbO,PbCl. This oxychloride has been used to some extent as a pigment instead of white lead. Another oxychloride (PbCl, 7 PbO) is a pigment of some importance, known under the name of *patent yellow*, or *Turner's yellow*; it forms a very fusible compound of a bright yellow colour, which may be obtained by heating together 1 part of sal ammoniac and 10 parts of litharge.

When an acid solution of chloride of lead is precipitated by a current of sulphuretted hydrogen, the precipitate which is first formed is of a bright red colour, but by the further action of the gas it becomes black, and furnishes sulphide of lead: the red compound is a *chlorosulphide* of lead (3 PbS, 2 PbCl).

Bromide of Lead (PbBr = 183·6; *Sp. Gr.* 6·63) is white, sparingly soluble, and fusible at a red heat.

(763) Iodide of Lead (PbI = 230·5; *Sp. Gr.* 6·384) is easily obtained by precipitating a solution of the nitrate or the acetate of lead by one of iodide of potassium; it is thrown down as a bright yellow powder, sparingly soluble in cold water, but more soluble in hot water; the solution as it cools deposits beautiful yellow spangles of a silky lustre; they may be fused by a moderate heat.

The iodide of lead forms double salts with the iodides of the alkaline metals. Several oxyiodides of lead may also be formed.

A remarkable compound of oxyiodide of lead with carbonate of lead (PbI,PbOI) + 4 (PbO,CO_2), of a blue colour, may be obtained by precipitating the tribasic acetate of lead with a mixture of 1 equivalent of biniodide of potassium and 4 equivalents of carbonate potash.

Fluoride of Lead (PbF) is white, insoluble, and fusible.

(764) *Sulphate of Lead*, (PbO,SO_3 = 151·6; *Sp. Gr.* 6·30).—This compound occurs native in white, prismatic, or octohedral crystals; it is also found in combination with carbonate of lead. When procured artificially, it forms a white powder, slightly soluble

in nitric acid, freely so in a solution of acetate of ammonia of sp. gr. 1·060, or upwards. An excess of sulphuric acid, however, throws down the whole of the lead as sulphate from the acetic solution. The other salts of ammonia also possess the property of dissolving sulphate of lead, but to a smaller extent. They form double salts with the sulphate of lead, and these compounds are slightly soluble. Sulphate of lead is dissolved also, to some extent, by concentrated sulphuric acid, but it is insoluble in pure water. Hot hydrochloric acid also dissolves it sensibly, and deposits crystals of chloride of lead on cooling, leaving a portion of sulphuric acid free in the solution. 100 parts of the salt contain 73·61 of oxide of lead and 26·39 of sulphuric acid. It may be obtained by adding sulphuric acid, or a solution of any sulphate, to a solution of one of the salts of lead. It is furnished in large quantities as a secondary product during the preparation of acetate of alumina. Like all the insoluble compounds of lead, it is gradually decomposed by sulphuretted hydrogen; a black sulphide of lead is formed and the acid is set free. Before the blowpipe it yields metallic lead in the reducing flame, though it will bear a high temperature without decomposition when heated alone. . Sulphate and sulphide of lead when heated together decompose each other, as explained when speaking of the process of lead smelting (751). The sulphate is reduced when heated with carbon, but the products vary with the proportion of carbon used, as may be seen by the annexed equations:—

$$2\,(PbO,SO_3)+C=2\,PbO+CO_2+2\,SO_2$$
$$PbO,SO_3+C=Pb+CO_2+SO_2$$
$$PbO,SO_3+4\,C=PbS+4\,CO$$

Sulphite of Lead (PbO,SO_2) is a white powder insoluble in water, but soluble in acids with escape of sulphurous acid: when heated it is partially decomposed, with escape of sulphurous acid.

(765) NITRATES OF LEAD.—Oxide of lead combines with nitric acid in several proportions, viz., PbO,NO_5; $2\,PbO,NO_5$; $3\,PbO,NO_5$, and $6\,PbO,NO_5$.

Nitrate of Lead ($PbO,NO_5=165·6$; *Sp. Gr.* 4·581).—This salt is easily formed by dissolving litharge or metallic lead in excess of nitric acid somewhat diluted; it crystallizes in regular anhydrous octohedra, which are sometimes transparent, but more commonly milk white and opaque: they contain 67·22 per cent. of oxide of lead, and 32·78 of nitric acid. It is soluble in about 8 parts of cold water, is sparingly soluble in nitric acid, and insoluble in alcohol. If heated to redness, it decrepitates strongly,

then fuses and is decomposed; oxygen, and peroxide of nitrogen (NO_4), in the anhydrous state, are evolved (309), while protoxide of lead remains. Caustic ammonia, if added to a solution of the nitrate, in quantity insufficient to combine with the whole of the acid, throws down a sparingly soluble *dinitrate of lead* ($2\,PbO, NO_5$). This salt may be also procured by boiling the normal nitrate with litharge. It is said to be deposited from its solution in hot water, in small opaque anhydrous crystals, which decrepitate forcibly when heated; I have, however, always found it to crystallize in leaflets with 1 Aq, and this accords with Péligot's observation. By precipitating the nitrate with a slight excess of ammonia, a *trisnitrate* is formed, which falls as a white powder, containing $1\frac{1}{2}$ Aq; by adding a large excess of ammonia to the normal nitrate, a *hexanitrate* is formed; it also contains $1\frac{1}{2}$ Aq (Berzelius).

(766) NITRITES OF LEAD.—The action of metallic lead on a solution of the nitrate of lead is remarkable; the acid of the normal salt imparts oxygen to the metal, which is dissolved, whilst subsalts of the lower oxides of nitrogen are produced. Several of these compounds may be obtained; the composition of the subsalt varying according to the proportions of the normal nitrate and of the metal employed. When a solution of 166 parts or 1 equivalent of nitrate of lead, is heated to about 140°, with 104 parts or 1 equivalent of metallic lead, perfect solution takes place, and a salt having the formula ($2\,PbO,NO_4+Aq$), or more probably ($2\,PbO,NO_5, 2\,PbO,NO_3+2\,Aq$), crystallizes on cooling, in yellow plates; for $PbO,NO_5+Pb=2\,PbO,NO_4$. If $1\frac{1}{2}$ equivalent of lead be employed instead of 1 equivalent, another salt, composed of ($7\,PbO,HO, 2\,NO_4+2\,Aq$), or, as is more probable, ($4\,PbO,NO_5+HO,3\,PbO,NO_3+2\,Aq$), crystallizes in heavy orange-red needles. By boiling a very dilute solution of the nitrate with 2 equivalents of lead for some time, a third salt, which is a *tetranitrite of lead*, composed of ($4\,PbO,NO_3+Aq$; Péligot), crystallizes in hard rose-red silky needles, which are but sparingly soluble in hot water, and still less so in cold: a normal nitrite of lead, PbO, NO_3, may be formed by transmitting a current of carbonic acid through the solution of the basic nitrite just mentioned: a dibasic nitrite, $2\,PbO,NO_3,HO$, as well as a tribasic nitrite, $3\,PbO, NO_3$, have also been formed.

(767) PHOSPHATES OF LEAD.—The salts of lead give a white precipitate with the soluble salts of each modification of phosphoric acid; these phosphates are principally interesting as furnishing an easy means of procuring the hydrates of these different

acids, by suspending the corresponding salt in water, and decomposing it by means of a current of sulphuretted hydrogen. All the phosphates of lead are soluble in nitric acid. The *diphosphate of lead* ($2\ PbO,PO_5$), before the blowpipe, furnishes a semi-transparent globule, which becomes remarkably crystalline on cooling. *Triphosphate of lead* occurs both massive and crystallized in six-sided prisms; the produce of a small mine at Wissembourg consists principally of this compound, mixed with the carbonate of lead. A *chlorophosphate of lead*, $PbCl + 3\ (3\ PbO,PO_5)$, is found native in yellow six-sided prisms: it is readily fusible.

Boracic acid may be fused with oxide of lead in all proportions; borate of lead enters into the composition of Faraday's optical glass. The *silicates of lead* enter largely into the formation of flint glass. Silica and oxide of lead may be fused together in almost all proportions; the larger the proportion of silica the less fusible is the compound, and the freer from colour: with an excess of oxide the glass is yellow.

(768) CARBONATES OF LEAD.—Native carbonate of lead (PbO, CO_2: *Sp. Gr.* 6·46) is a beautiful mineral met with crystallized in transparent needles, or in fibrous masses, which are generally opaque. It is soft and brittle, and usually accompanies the deposits of galena, in small quantity. The manufacture of carbonate of lead, or *white lead* for the painter, is carried on upon a large scale. Several methods are in use in the preparation of this compound: in all of them, however, certain peculiarities in the properties of the acetates of lead are taken advantage of. There are two acetates of lead, a normal salt, $PbO,C_4H_3O_3$, and a tribasic acetate, $3\ PbO,C_4H_3O_3$. A solution of the normal acetate in the presence of an excess of oxide of lead readily unites with it to form the basic salt, and this subacetate, if exposed to an atmosphere containing carbonic acid, rapidly absorbs this gas, and is thus converted into carbonate of lead and normal acetate. These changes may be thus represented:—

$$\overbrace{PbO,C_4H_3O_3}^{\text{Acetate of Lead.}} + 2\ \overbrace{PbO}^{\text{Ox. Lead.}} = 3\ \overbrace{PbO,C_4H_3O_3}^{\text{Triacetate of Lead.}};\ \text{and}$$

$$3\ \overbrace{PbO,C_4H_3O_3}^{\text{Triacetate of Lead.}} + 2\ \overbrace{CO_2}^{\text{Carb. Acid.}} = \overbrace{PbO,C_4H_3O_3}^{\text{Acetate of Lead.}} + 2\ \overbrace{(PbO,CO_2)}^{\text{Carbonate of Lead.}}.$$

The following is the plan which is known as the Dutch method of making white lead; it is still carried on extensively at Lille:— A number of small glazed earthen pots are partially filled with a weak malt vinegar, and in each pot a thin sheet of cast lead coiled

into a spiral form is placed; these pots are each covered with a plate of lead, and arranged in rows; they are then placed in tiers one above another to a depth of 18 or 20 feet, and imbedded in spent tan or in decomposing horse-dung; the warmth given out during its putrefaction volatilizes the vinegar, and, under the united influence of the air and acid fumes, an oxide of lead is formed upon the surface of the coils of metal; this oxide combines with the acetic acid which rises in vapour from the vinegar, and a basic acetate of lead is thus produced. The carbonic acid which is supplied from the decomposing hot-bed readily converts this salt into carbonate of lead and the normal acetate; whilst the latter again combines with a fresh portion of newly-formed oxide, and produces the subacetate, which is decomposed as before: successive decompositions and recompositions ensue, as the normal acetate immediately dissolves any oxide of lead presented to it, forming the subacetate, which again is decomposed under the influence of carbonic acid. Rolled lead cannot be advantageously substituted for cast lead in this process (Brande), and the purest lead is always preferred, traces of iron being sufficient to impart an objectionable yellow tinge to the product.

Since the lead in this process derives oxygen from the air, it is necessary that the atmosphere be allowed to come sufficiently into contact with the coils. The quantity of vinegar which is required is very small, 1 part of pure acetic acid to 100 parts of lead being amply sufficient. The carbonate is thus produced very slowly, and forms a compact layer upon the surface of the coils. It always contains an excess of hydrated oxide of lead, but the proportion of this oxide is liable to vary. Mulder found a specimen which he examined, to contain $PbO,HO+3\,(PbO,CO_2)$; but more usually it consists of $PbO,HO+2\,(PbO,CO_2)$. By unrolling the coils, the carbonate breaks off in flakes of a dead-white colour, furnishing the kind of white lead most approved by artists and colourmen. Before it is fitted for their use, it is subjected to the processes of grinding and levigation, by which it is reduced to an impalpable powder. Although this pulverization is performed under water, the fine particles of the carbonate become diffused through the air, rendering the operation very deleterious to the workmen.

This circumstance, combined with the length of time requisite for the formation of the carbonate, induced Thénard to substitute for the foregoing process the direct decomposition of a solution of the subacetate of lead, by means of a current of carbonic acid: the carbonate is thus procured in a state of extreme division, and as rapidly as can be desired: it has, however, less opacity, or body,

owing to its being deposited in exceedingly minute crystals, and is inferior as a pigment to that procured by the Dutch method.

A third process, at one time employed at Birmingham, consisted in exposing litharge, moistened with a solution of acetate of lead, to a current of impure carbonic acid, obtained from the combustion of coke.

Carbonate of lead is easily decomposed by heat, giving off carbonic acid, and leaving a residue of protoxide of lead. It is insoluble in water, unless the water be charged with carbonic acid to a large extent, when it is slightly soluble. It is also soluble in most of the acids with effervescence, and is likewise dissolved by solutions of potash and soda. It is quickly blackened by exposure to sulphuretted hydrogen both in the form of gas and when in solution in water. This liability to blacken by the action of the gas possessed by the carbonate in common with all the salts of lead, is a serious objection to the use of the compounds of lead in pigments.

Carbonate of lead is often fraudulently mixed with a considerable quantity of sulphate of baryta, which is much cheaper, though its whiteness is less intense; a small quantity of indigo, charcoal, or sulphide of lead is usually added to white lead, in order to substitute a bluish tint for the natural tendency of the white towards yellow.

(769) Characters of the Compounds of Lead.—The salts of lead with colourless acids are colourless. The soluble salts, even when neutral in composition, redden litmus; but its basic salts have an alkaline reaction. They have a sweetish metallic taste and exert a poisonous action on the system. In cases of poisoning by a dose of the soluble salts of lead, the best antidote is sulphate of magnesia, or of soda, which forms an insoluble and inert sulphate of lead. This, however, is of no avail in the more usual forms of lead poisoning, in which the metal is introduced in minute quantities, unintentionally, in water, or in articles of diet.

The best tests for lead are the formation of a white insoluble sulphate when *sulphuric acid* or any of the soluble *sulphates* are added to its solutions; a black sulphide with *sulphuretted hydrogen* and with *hydrosulphate of ammonia*, insoluble in excess of the precipitant; a yellow chromate with *chromate of potash;* and a yellow iodide with *iodide of potassium*. *Hydrochloric acid* and the soluble chlorides give in moderately diluted solutions of lead, a white crystalline precipitate of chloride of lead, readily soluble in excess of potash. *Potash* gives a white precipitate of the

hydrated oxide, which is redissolved in an excess of the fixed alkalies, but is nearly insoluble in ammonia. *Carbonate of potash*, or of *soda*, gives a dense white precipitate of white lead, which is insoluble in excess of the precipitant. Many other insoluble white salts may be formed, as the phosphate, arseniate, the ferrocyanide, and the cyanide: the latter is insoluble in excess of cyanide of potassium, but soluble in diluted nitric acid. All the insoluble salts of lead are soluble in a solution of potash. Lead has a remarkable tendency to form subsalts, but the number of its double salts is not great. From the insolubility of many of its organic compounds, it has been much used to determine the combining proportion of organic bodies. It is, however, more advantageous to employ the oxide of silver for this purpose, because the oxide of lead is to a small extent volatile.

Lead, like most other metals of comparatively weak affinity for oxygen, is easily precipitated from its solutions in the metallic state, by the metals more oxidable than itself: if, for instance, a piece of zinc be suspended in a solution containing lead, crystals of lead are deposited in a beautiful arborescent form.

Before the blowpipe on charcoal the salts of lead yield a soft white malleable bead of the metal, surrounded by a yellow ring of oxide.

(770) *Estimation of Lead.*—Lead is generally estimated in the form of the sulphate, which contains 68·31 per cent. of the metal. More rarely it is determined from the protoxide, of which 100 parts correspond to 92·82 of lead : porcelain crucibles must be employed for these experiments, since oxide of lead is easily reduced to the metallic state, in which case it would form an alloy with platinum, and would ruin a crucible composed of this metal.

Lead may be separated by means of sulphuric acid from all the metals, except its insoluble combinations with the metallic acids. The following is the method to be adopted:—If a galena or an alloy of lead is to be analysed, it should be treated with concentrated nitric acid until it is completely decomposed, and then evaporated nearly to dryness with a small excess of sulphuric acid; the nitric acid is thus expelled, and the metals are converted into sulphates; the mass is treated with water, which dissolves out all the metals except lead, tin, and antimony: quartz, or sulphate of baryta, if present, would also be contained in this insoluble portion. The insoluble residue is collected and weighed, and then digested repeatedly in a solution of acetate of ammonia, of sp. gr. 1·065; after which the residue is again washed, dried, and weighed: the difference indicates the proportion of sulphate of lead which is dis-

solved out from the oxides of antimony and tin, and from the quartz and sulphate of baryta. The lead may be obtained from its solution in the acetate of ammonia by the addition of hydrosulphate of ammonia: and the sulphide of lead thus precipitated may be converted into sulphate by means of a mixture of nitric and sulphuric acids. It is evaporated down to dryness, ignited, dried, and weighed.

The salts of lead with the metallic acids may be decomposed by fusing them with a mixture of caustic potash and carbonate of potash: the metallic acid combines with the potash, and may be dissolved by the addition of water, and a portion of the oxide of lead is left.

CHAPTER XVII.

GROUP VII.—THE NOBLE METALS.

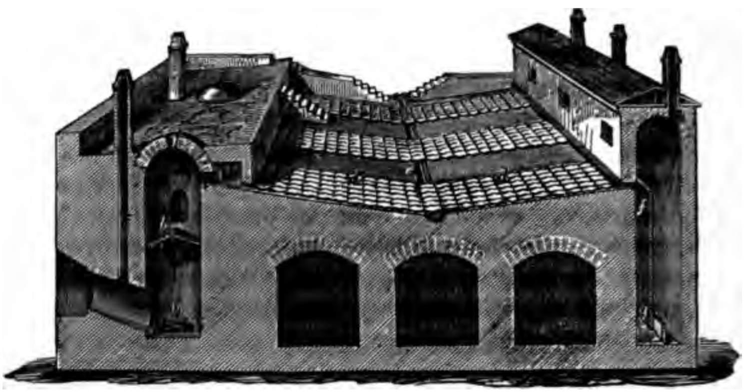
§ I. MERCURY (Hg=100). *Sp. Gr. as liquid* at 32° F., 13·596, *as vapour*, 6·976; *Comb. Vol.* 2.

(771) MERCURY or *Quicksilver* is one of the metals which have been longest known; it is found in but few localities, and occurs most frequently in the form of the sulphide (cinnabar), usually accompanied with small quantities of the metal in its native state. Occasionally it is met with combined as an amalgam with silver, and sometimes in the form of subchloride or calomel, and more rarely in the form of iodide. Generally speaking, its ores are found in clay-slate, or in the red sandstone underlying the coal, and not unfrequently among the coal measures themselves. The most productive mines are those of Almaden, in Spain; very extensive and valuable deposits of cinnabar have likewise been lately found in California; and the mines of Idria, in Transylvania, have also been extensively worked. Considerable quantities are likewise raised in China and Japan, and from the mine of Huancavelica, in Peru.

Extraction.—The metal may be obtained from its ore either by burning off the sulphur and distilling the mercury,—a process which applies both to cinnabar and to the native metal; or by heating the cinnabar with some substance capable of combining with the sulphur, and forming a fixed compound, from which the mercury is separated by heat. At Almaden, the metal is extracted

by the first process. The ore employed yields about 10 per cent. of mercury. Fig. 336 shows a section of the furnace employed:— each furnace contains two grates, and on the lower one, *a*, provided with a chimney, *i*, a fire of brushwood is kindled; the upper grating is formed by a brick arch, *b*, perforated with numerous apertures; on this arch the sulphide rests, the poorer pieces of ore being placed at the bottom. The brushwood quickly kindles the sulphur in the ore, which afterwards by its combustion maintains sufficient heat to continue the operation without the use of any

FIG. 336.



other fuel: sulphurous acid is formed, and the liberated mercury distils, and is condensed in wide earthen pipes, *d*, *d*, connected with the upper aperture, *c*, of the furnaces; these pipes are termed *aludels*. The aludels are supported on a doubly inclined plane of masonry; at the lowest point a perforation is made, to allow of the escape of the mercury into a brick channel, *e*, through which it runs into a well; the further end, *f*, of the aludels opens into a condensing chamber, in which an additional quantity of mercury is deposited in the trough, *g*: the sulphurous acid escapes into the air, through the chimney, *h*. Considerable waste of metal is incurred during this process, from the incomplete manner in which the condensation is effected. Iron pipes, however, cannot be substituted for the earthen ones, as they become corroded rapidly by the acid vapours produced in the operation.

At Idria the process of extraction is the same in principle as at Almaden, but the condensation is effected more completely by transmitting the mercurial vapours through a succession of chambers of masonry, instead of through aludels.

Another plan which is practised in the Palatinate consists in mixing the sulphide with slaked lime, and conducting the distil-

lation in cast-iron furnaces and retorts. The mercury is condensed in receivers partly filled with water, while sulphide of calcium and sulphate of lime remain behind in the retort: $4\,HgS + 4\,CaO = 4\,Hg + 3\,CaS + CaO,SO_3$. Iron filings also decompose cinnabar when heated with it, sulphide of iron being formed while mercury is liberated. Experience has shown that unless the ore contain at least $\frac{1}{600}$ of its weight of the metal, or 3·8 lb. per ton, it is too poor to be advantageously worked by the methods at present in use.

Purification.—If the ore contain any admixture of zinc and bismuth, small portions of these metals are liable to be distilled over with the mercury. In this case a film forms upon the surface of the fluid metal when it is agitated in contact with air. The purity of the product is easily seen by the absence of this film, and by the perfect mobility and sphericity of the globules, which do not wet the surface of non-metallic objects. Violette finds that the distillation of mercury on the large scale is much facilitated by transmitting a current of superheated steam at about 700° through the retort in which the distillation is being effected. A small quantity of mercury may be speedily purified by placing it in a bottle, with a little finely powdered loaf-sugar; the mercury should not occupy more than one fourth of the capacity of the bottle: the bottle is then closed, and briskly agitated for a few minutes; after which the stopper is withdrawn, and fresh air is blown into the bottle with a pair of bellows, and the agitation is repeated; this is done three or four times, and the mercury is then poured into a cone of smooth writing paper, in the apex of which a pin hole is made; the metal runs through, and leaves the powdered sugar mixed with the oxides of the foreign metals, and a considerable quantity of finely divided mercury.

Generally speaking, the mercury imported into this country is almost chemically pure. Any foreign metals which may be present in it may be removed by digesting it for some days with diluted nitric acid in the cold: the mercury should be placed in a shallow dish, so as to expose a large surface to the acid, and it should be frequently agitated; the acid exerts but little action on the mercury so long as any more oxidizable metals are present. A solution of nitrate of mercury may be substituted for the nitric acid with advantage; in this case the mercury is deposited from the solution and takes the place of the other metals, which are dissolved.

(772) *Properties.*—Mercury possesses a lustre resembling that of polished silver. It is the only metal that is fluid at common

temperatures. It freezes at —39° F., and contracts considerably at the moment of congelation, when it crystallizes in octohedra, of sp. gr. about 14: in this state it is malleable. When heated to 662° it boils, and forms an invisible, transparent vapour, of sp. gr. 6·976. The metal, at all temperatures above 40°, undergoes slight spontaneous evaporation. Its specific gravity at 60° is 13·54. When pure, it is not tarnished by exposure to air and moisture at ordinary temperatures, but if heated to about 700° or 800° it absorbs oxygen, and is gradually converted into the red oxide. Mercury enters into combination with chlorine, bromine, and with many of the metals at ordinary temperatures. It also unites with sulphur and with iodine without the aid of heat, if triturated with them. Hydrochloric acid is without action upon the metal, either when cold or hot. Hydriodic acid and sulphuretted hydrogen are decomposed slowly by it, with evolution of hydrogen. Concentrated sulphuric acid in the cold produces no change, but when heated with it is decomposed; sulphurous acid being evolved, while the mercury is oxidized and combines with a portion of undecomposed acid. Strong nitric acid dissolves it with rapidity, extricating deutoxide of nitrogen in abundance, while nitrate of mercury is formed. If the acid be dilute, and the metal in excess, the mercury is dissolved slowly, and at ordinary temperatures the nitrate of the suboxide is the result. Mercury may be obtained in a state of extreme division, by precipitating a solution of corrosive sublimate, by means of the solution of protochloride of tin: the chloride of tin, if added in sufficient quantity, absorbs all the chlorine, and a grey metallic powder subsides; $HgCl + SnCl = Hg + SnCl_2$.

Uses.—Mercury is employed extensively in the extraction of gold and silver from their ores, by the processes of amalgamation; great quantities are annually sent to South America for this purpose. Its amalgams are largely employed in the processes of silvering and gilding. Mercury also combines readily with lead, copper, bismuth, tin, and zinc, forming amalgams which are easily dissolved by an excess of mercury. Joule succeeded in many cases in obtaining definite compounds of various metals with mercury, by subjecting their semi-solid amalgams to hydraulic pressure, amounting to the enormous extent of 60 tons upon the square inch: with platinum and with silver, 1 atom of each of these metals were united with 2 atoms of mercury. With copper and with iron, the amalgams contained 1 atom of each metal: with zinc and with lead the amalgam in each case contained 1 atom of mercury with 2 atoms of the other metals, while the amalgam of tin was represented by the formula Sn_7Hg.

Mercury is also used in the preparation of vermilion, which is highly valued as a pigment, for the purity and permanence of its tint. It is indispensable in the construction of philosophical instruments; and it is well known in various forms as an invaluable medicine. It exerts a powerful action upon the animal economy, producing salivation, and seriously impairing the health of the workmen exposed to its vapours, giving rise to a remarkable tremulous state, known as *mercurial palsy*, consequent upon a peculiar form of nervous debility. By trituration with saccharine or oleaginous substances, it admits of being minutely subdivided, and a small portion of it becomes oxidized, to which the active properties of blue pill appear to be owing: the same remark applies to the mercurial ointment, and the *pulvis hydrargyri cum cretâ*.

(773) OXIDES OF MERCURY.—Mercury forms two oxides, the black suboxide, Hg_2O, and the red oxide, HgO: both of them form salts with acids.

Suboxide of Mercury; Mercurous Oxide ($Hg_2O=208$; *Sp. Gr.* 10·68).—This oxide, though a powerful saline base, is very unstable when isolated. It is best procured by triturating finely levigated calomel with a solution of potash or of soda, and washing the black precipitate thus obtained with cold water. It must be allowed to dry spontaneously in a dark place; even when dry, mere exposure to light, or a very gentle heat, is sufficient to convert it into red oxide and the metal.

(774) *Nitric Oxide, Mercuric Oxide*, or *Red Oxide of Mercury* ($HgO=108$; *Sp. Gr.* 11·29).—This oxide may be obtained in red scales by heating metallic mercury to 700° or 800° in a matrass: but this process is very slow, and not productive: it is more conveniently prepared by the decomposition of the nitrate by heat, and it then has a bright orange colour. It may also be thrown down in the form of a yellow powder, when potash or soda is added to a solution of corrosive sublimate, or of nitrate of mercury. The precipitated oxide does not differ in composition from the red crystallized form, but it enters more readily into combination; a cold solution of oxalic acid is without action on the crystallized oxide, but it converts the precipitated oxide into oxalate, and the yellow oxide when boiled with a solution of corrosive sublimate, is quickly converted into the oxychloride; but this change is very slow with the crystallized variety. The yellow oxide, when boiled with bichromate of potash, yields a subchromate of mercury, $3\,HgO,CrO_3$; but the crystallized oxide when similarly treated, yields subsalt with a larger excess of base, $4\,HgO,CrO_3$ (Millon).

In short, the crystallized oxide obtained by the direct oxidation of mercury and the precipitated oxide appear to be in different allotropic conditions.

The red oxide when heated becomes nearly black, but recovers its colour on cooling; when exposed to a temperature of ignition, it is decomposed into metallic mercury and oxygen gas: owing to the volatility of the metal, this oxide may sometimes be usefully employed as an oxidizing agent in some analytical operations. 100 parts of the red oxide of mercury contain 92·59 of the metal and 7·41 parts of oxygen. This oxide is slightly soluble in water; the solution has an acrid taste, and turns syrup of violets green. It forms with baryta a soluble compound. With ammonia it produces a yellowish-white insoluble compound ($Hg_4H_5NO_6$) possessed of strong basic powers; it enters into combination with acids, and forms well-defined salts.

(775) The best method of preparing this remarkable base consists in pouring a solution of ammonia upon yellow precipitated oxide of mercury in a bottle which admits of being closed, to prevent the access of carbonic acid from the air; the colour of the oxide becomes paler, and eventually a yellowish-white amorphous powder is obtained, which, when washed and dried in a dark place, over quicklime, forms a hydrate of the new base, containing ($Hg_4H_2NO_3$, 3 HO). This compound was discovered by Fourcroy and Thénard, but it was first minutely examined by Millon (*Ann. de Chimie*, III., xviii. 393). In its isolated condition, it is very unstable: mere exposure to the light decomposes it. When triturated in a mortar, it produces a series of small detonations. If dried *in vacuo* over sulphuric acid, it loses two equivalents of water; and between 212° and 266°, a third equivalent of water is expelled: it then becomes dark brown, and is permanent in the air, containing ($Hg_4H_2NO_3$). Chemists are not agreed as to the probable arrangement of the elements in this base. It resembles some of the cobalt bases into the composition of which the elements of ammonia enter. It may provisionally be described under the name of *mercuramine*, and contains the elements of hydrated oxide of *tetrhydrargammonium* ($Hg_4NO + 5HO$).

Mercuramine is a powerful base; its hydrate ($Hg_4H_2NO_3$, 3 HO) absorbs carbonic acid from the air almost as rapidly as slaked lime. It is insoluble in water and in alcohol, but it decomposes solutions of the salts of ammonia and combines with the acid. Definite salts with sulphuric, nitric, oxalic, carbonic, hydrochloric, and various other acids have been formed. On the addition of soda or potash to the solutions of these salts, the hydrate of the base is

precipitated. The formula of the sulphate is $(Hg_4H_2NO_2)\ O,SO_3$; that of the chloride $(Hg_4H_2NO_2)\ Cl$; the latter salt may be obtained as a yellow precipitate, by adding a solution of corrosive sublimate to a solution of ammonia in excess, and washing the precipitate with boiling water (781).

(776) SULPHIDES OF MERCURY.—The two sulphides of mercury, Hg_2S, and HgS, correspond in composition to the oxides and chlorides of the metal.

Subsulphide of Mercury ($Hg_2S=216$), is scarcely more stable than the suboxide of the metal; it is procured by transmitting a current of sulphuretted hydrogen through a solution of a mercurial subsalt, or by triturating 16 parts of moistened sulphur with 200 of mercury; it forms a black powder, which was formerly termed *Ethiop's mineral.* It is decomposed by nitric acid; and if the dry sulphide be sublimed, it is converted into cinnabar and metallic mercury.

(777) *Sulphide of Mercury,* or *Cinnabar* ($HgS=116$; *Sp. Gr. of vapour,* 5·51; *of solid,* 8·2; *Comb. Vol.* 3).—This compound constitutes the most abundant ore of mercury. It occurs sometimes crystallized in hexahedral prisms, but more usually as a fibrous or amorphous mass, and is a product of considerable importance in the arts, forming the pigment known under the name of *vermilion.* Some portions of the native cinnabar are of a sufficiently delicate colour to be employed after mere levigation; but it is usually prepared artificially. In Holland, this manufacture is carried on to a considerable extent. The process adopted consists in triturating sulphur with about 6 times its weight of mercury, aiding the action by a gentle heat. The black mass thus procured is thrown (in successive portions, to prevent too rapid an action) into tall earthen pots, the lower parts of which have been previously brought to a red heat; the aperture at top is closed with an iron plate, and in about 32 hours after the introduction of the whole charge, the sublimation is complete: when cold, the pots are broken, and the cinnabar, which is found deposited in layers upon the upper part, is carefully removed; the cinnabar is levigated with water, and the fine powder thus obtained is sold as vermilion; an excess of sulphur is to be avoided, as it impairs the brilliancy of the colour. Cinnabar sublimes before undergoing fusion, and forms a yellowish-brown vapour. Vermilion may also be procured in the wet way, but the process is tedious, and less certain. The Chinese vermilion is supposed by some chemists to be prepared by the humid process. In order to produce vermilion by this means, Brunner recommends the mercury to be subjected

to the action of a polysulphide of one of the alkaline metals in the following manner:—100 parts of mercury are to be triturated, for 2 or 3 hours, with 38 parts of sulphur; at the end of which time, 25 parts of caustic potash, and 150 parts of water are to be added. The mixture is maintained for some hours at a temperature of from 112° to 120°, at first stirring it constantly: the black colour gradually changes to scarlet; as soon as it has attained the desired tint, it is thoroughly washed with cold water. If the heat be too long continued, the tint changes to brown, but the scarlet hue is restored by boiling it with water. 100 parts of cinnabar contain 86·21 of mercury, and 13·79 of sulphur.

Sulphide of mercury is thrown down as a black precipitate by transmitting sulphuretted hydrogen through solutions of the per-salts of mercury: when dried and sublimed in vessels from which air is excluded, it assumes its ordinary red colour. When heated in the open air, the sulphur burns off, and metallic mercury is liberated. It is upon this circumstance that the ordinary method of extracting the metal is founded. The pure acids are nearly without action upon it, but it is oxidized and dissolved by aqua regia. The alkalies in solution do not decompose cinnabar, but if ignited with it in the dry state, a sulphate and sulphide of the alkaline metal are formed, and metallic mercury sublimes; $4\ HgS + 4(KO,HO) = 4\ Hg + KO,SO_3 + 3\ KS + 4HO$. It is also decomposed if heated with metals which, like iron, zinc, and copper, have a powerful affinity for sulphur. Sulphide of mercury possesses the property of uniting with other metallic sulphides, but is not soluble in a solution of sulphide of potassium; it also combines with the nitrate, the chloride, the iodide, and some other mercurial salts, forming peculiar compounds, which are produced by the action of a small proportion of sulphuretted hydrogen upon the solutions of these salts, and cause the first portions of the precipitate occasioned in them by the gas to assume a white colour.

(778) CHLORIDES OF MERCURY.—Mercury forms two chlorides, a subchloride, Hg_2Cl, well known as calomel, and a chloride, $HgCl$, commonly distinguished as corrosive sublimate.

Subchloride of Mercury, Mercurous Chloride ($Hg_2Cl = 235{\cdot}5$; *Sp. Gr. of vapour*, 8·35; *of solid*, 7·178), or *Calomel*, may be obtained by precipitating the subnitrate of mercury by means of a solution of common salt; but it is more usually procured by sublimation: 13 parts of mercury are triturated with 17 of corrosive sublimate, until no metallic globules are visible, the chloride having been previously moistened with water or alcohol to prevent the acrid particles from being diffused through the air; the mixture is then

sublimed in suitable vessels, and the calomel is deposited as a semi-transparent fibrous cake. In this operation the additional mercury combines with half the chlorine of the chloride; $HgCl + Hg = Hg_2Cl$. Sometimes the vapours are sent into a capacious chamber; the deposit then assumes the form of a fine powder. The salt may also be obtained by the decomposition of sulphate of mercury with chloride of sodium. For this purpose the London pharmacopœia directs 2 lb. of mercury to be converted into sulphate by boiling it to dryness with 3 lb. of sulphuric acid; the residue is then to be intimately mixed with 2 lb. more of mercury, and subsequently triturated with 1½ lb. of chloride of sodium, after which it is to be sublimed. The sulphate of red oxide of mercury which is first obtained is converted into sulphate of the suboxide by the addition of the second portion of mercury, and this in its turn is decomposed into calomel and sulphate of soda when heated with chloride of sodium:—

$$HgO,SO_3 + Hg = Hg_2O,SO_3\text{; and}$$
$$Hg_2O,SO_3 + NaCl = NaO,SO_3 + Hg_2Cl.$$

Calomel may also be prepared by forming a saturated solution of corrosive sublimate in water at 120°, and transmitting sulphurous acid into the hot liquid; calomel is then precipitated in minute crystals, whilst sulphuric and hydrochloric acids are liberated:—

$$2\,HgCl + 2\,HO + SO_2 = Hg_2Cl + HCl + HO,SO_3.$$

When prepared by sublimation calomel requires careful washing and levigation, because portions of the undecomposed chloride always sublime with the calomel, and they can only be removed by repeated washing. It was formerly supposed that the medical character of calomel was rendered milder by repeated sublimations. This, however, has been found to be a serious mistake, for every time that calomel is sublimed, a small portion of it is reconverted into corrosive sublimate and metallic mercury. 100 parts of calomel contain 84·92 of mercury and 15·08 of chlorine.

Properties.—Calomel sublimes in quadrilateral prisms terminated by four-sided pyramids; when powdered it is of a yellowish-white colour. It begins to sublime below redness, and before undergoing fusion. Calomel is tasteless and insoluble in water; the alkalies decompose it. Soda and potash set free the suboxide. Lime-water has a similar effect, and when mixed with a small proportion of calomel it furnishes what is known as *black wash*. Solution of ammonia forms with calomel a black compound, consisting of Hg_4H_2NCl: this change is explained in the subjoined equation;

$2\ Hg_2Cl + 2\ H_3N = Hg_4H_2NCl + H_4NCl$. This black compound may be regarded as muriate of ammonia in which two double atoms of mercury have taken the place of two atoms of hydrogen $(Hg_2)_2H_2NCl$. Ammoniacal gas is absorbed by calomel at ordinary temperatures, and a compound containing (Hg_2Cl,H_3N) is formed. Sulphuric acid is without action on calomel; boiling nitric acid dissolves it, and forms corrosive sublimate and nitrate of mercury; a solution of chlorine converts it slowly into corrosive sublimate; if boiled for a long time with hydrochloric acid or chloride of sodium, it is resolved into corrosive sublimate and metallic mercury: the same effect is produced, but more rapidly, by boiling it in a solution of sal ammoniac.

(779) *Chloride* (formerly *Bichloride*) *of Mercury*; *Mercuric Chloride* or *Corrosive Sublimate* (HgCl = 135·5; *Sp. Gr. of vapour*, 9·8; *of solid*, 6·223).—When heated mercury is placed in an atmosphere of chlorine it ignites from the rapid union of the gas with the metal, and the chloride is formed. It is prepared on the large scale by mixing intimately 2½ parts of sulphate of mercury with 1 part of common salt, and subliming the mixture in glass vessels at a carefully regulated heat: sulphate of soda remains in the vessel, and the chloride sublimes, as represented in the equation; $HgO,SO_3 + NaCl = NaO,SO_3 + HgCl$. The fumes are extremely acrid and poisonous. 100 parts of this salt contain 73·8 of mercury and 26·2 of chlorine.

Corrosive sublimate fuses at 509° and boils at 563°; its vapours are condensed in snow-white crystalline needles, or in octohedra with a rectangular base. As sold in the shops, it occurs in transparent colourless masses, which have a crystalline fracture. It has an acrid burning taste, and disgusting metallic flavour. It is soluble in 16 parts of cold water, and in less than 3 of boiling water; on cooling it is deposited from a concentrated solution in transparent anhydrous quadrilateral prisms. Its solution reddens litmus; this aqueous solution, by long exposure to light, is gradually decomposed, and calomel is deposited. Alcohol when cold dissolves nearly one third of its weight of the salt, and its own weight when boiling; ether also dissolves it freely. If an aqueous solution of corrosive sublimate be agitated with ether, almost the whole of the salt will be abstracted by it from the water, and the ethereal solution will rise to the surface. It is very soluble in solutions of the alkaline chlorides, with which it enters into combination, forming double salts. With chloride of potassium it forms three distinct crystallizable compounds, $KCl, 4\ HgCl + 4\ Aq$; $KCl,2\ HgCl + 2\ Aq$; and $KCl,HgCl + Aq$. They are easily prepared by dissolving the

salts in the proper proportions, and allowing them to crystallize. With chloride of sodium only one such compound is formed, $NaCl, 2\,HgCl + 3\,Aq$. A salt of ammonia with 3 equivalents of sal ammoniac ($3\,H_4NCl,HgCl + Aq$) has long been known as *sal alembroth*: it crystallizes in flattened rhomboidal tables.

Similar compounds having a composition analogous to that of the sodium salt may be formed with most of the soluble chlorides. Chlorides of calcium and magnesium form more than one compound. A similar but anhydrous salt, $HCl, 2\,HgCl$, is formed by dissolving corrosive sublimate in hot hydrochloric acid, from which it crystallizes on cooling; it is, however, decomposed by water.

Chloride of mercury combines with the sulphide, and forms with it a white insoluble gelatinous compound, consisting of $2\,HgS,HgCl$; it is the white precipitate which is always formed at first, on passing a current of sulphuretted hydrogen through a solution of corrosive sublimate.

Corrosive sublimate is decomposed by the fixed alkalies and alkaline earths; a chloride of the alkaline metal is formed, and oxide of mercury is set free. When ammonia is added to a solution of corrosive sublimate, it separates only half the chlorine, uniting with the remainder to form the compound called white precipitate. Chloride of mercury acts powerfully on the albuminous tissues, and combines with them; it is a violent and acrid poison. The best antidote in cases of poisoning with this substance is the immediate exhibition of the whites of several raw eggs, as it coagulates the albumen, and forms with it a sparingly soluble compound. It was supposed that the chloride was converted into calomel, but this does not appear to be the case. Owing to this action of the chloride upon albumen, corrosive sublimate is a powerful antiseptic; a solution of this salt is hence often employed to preserve anatomical preparations: wood, cordage, and canvas, if soaked in a solution of the salt containing 1 part of it in 60 or 80 parts of water become much less liable to decay when exposed to the combined action of air and moisture.

(780) *Oxychlorides.*—Corrosive sublimate combines with oxide of mercury in several proportions. One of these is obtained in the form of dark brown insoluble flakes, ($3\,HgO,HgCl$), when the chloride is boiled with red oxide of mercury; these compounds are decomposed by the alkalies. Another, $2\,HgO,HgCl$, is obtained in blackish scales by acting with a solution of chlorine on red oxide of mercury (Thaulow). The oxychlorides of mercury are interesting, from the observations of Millon upon them, which seem to prove the persistence of the allotropic modification in a body

after it has entered into combination. *Ann. de Chimie*, III., xviii. 333.

The three oxychlorides described by Millon consist of (2 HgO, HgCl), (3 HgO,HgCl), and (4 HgO,HgCl). They may all be produced by the action of bicarbonate of potash upon a solution of corrosive sublimate. The first may be obtained in three different isomeric conditions, the second in two, and the third in three. The action of the carbonates of the alkalies upon solutions of corrosive sublimate is peculiar. The addition of a solution of sublimate to a solution of pure *normal* carbonate of soda or potash is attended with the precipitation of yellow oxide of mercury. If the mercurial solution be added to a solution of an alkaline *bicarbonate*, a red oxychloride is formed; and if even a small quantity of bicarbonate of the alkali be mixed with a large proportion of normal alkaline carbonate, this red precipitate is produced at first. This reaction may serve to indicate the difference between carbonates and bicarbonates in solution. If a cold saturated solution of bicarbonate of potash be added gradually to 8 or 10 times its volume of a cold saturated solution of sublimate, a light granular amorphous precipitate of a bright brick-red colour is formed (2 HgO,HgCl). If the volume of the solution of sublimate be only 3 or 4 times as great as that of the bicarbonate, a precipitate of similar composition is formed, but it is dense, crystalline, and red, purple, or violet, in colour. Both these modifications, when decomposed by potash, yield the *yellow oxide* of mercury, but if 1 volume of the solution of bicarbonate be added to 2 volumes of the solution of sublimate, stirring briskly, a jet black crystalline precipitate is formed, which also consists of 2 HgO,HgCl, but which yields the *red crystalline oxide* when decomposed by potash.

If equal volumes of the solutions be mixed, golden-yellow plates, which gradually become brown or yellowish, are deposited, (HgCl, 3 HgO). The same body may also be obtained in the amorphous form.

The quadribasic oxychloride (4 HgO,HgCl) may be obtained by adding a solution of corrosive sublimate to a large excess of the solution of the bicarbonate. Carbonic acid gradually escapes, and brown crystalline crusts are deposited: caustic potash causes the separation of the *red oxide* of mercury from this compound. This oxychloride may also be obtained in the form of a brown amorphous deposit, and in golden-yellow plates; both these varieties yield the *yellow oxide* when decomposed by potash. The first two oxychlorides are converted by boiling them with water into the quadribasic form, which is deposited from the solution in golden-yellow

scales. Other oxychlorides with 5, and with 6 atoms of oxide of mercury are described by Roucher (*Ann. de Chimie*, III. xxvii. 353).

(781) *Action of Ammonia on Chloride of Mercury.*—When a solution of corrosive sublimate is added to a solution of ammonia in excess, one half of the chlorine only is removed from the salt, and a *white precipitate* is formed, which, when washed with cold water, is completely soluble in nitric and in hydrochloric acid, and which therefore can contain no calomel; $2\ HgCl + 2\ H_3N = (Hg_2H_2N,Cl) + H_4NCl$. Kane considers this white precipitate as a compound of chloride with amide of mercury, $HgCl,HgH_2N$; but it may also be regarded as chloride of ammonium, in which 2 equivalents of hydrogen are displaced by 2 equivalents of mercury (Hg_2H_2N,Cl). If ammonia be added drop by drop to a solution of corrosive sublimate, which is purposely maintained in considerable excess, the precipitate consists of (Hg_4H_2N,Cl_3); this formula would be that of chloride of mercuramine, in which the place of each atom of the oxygen contained in the base is supplied by an equivalent amount of chlorine.

White precipitate has been made the subject of numerous experiments. If it be heated to about 600°, ammonia and the ammoniated chloride of mercury are expelled; and a red crystalline powder remains, represented by the formula, $(2\ HgCl,Hg_3N)$; for $6\ (H_2Hg_2N,Cl) = 3\ H_3N + (H_3N,\ 2\ HgCl) + 2\ (2\ HgCl,Hg_3N)$. This red powder is insoluble in water and in dilute acids, but it is dissolved and decomposed by either boiling hydrochloric acid or oil of vitriol. By raising the temperature still further it is decomposed into nitrogen, metallic mercury and calomel. It is interesting, as it appears to contain ammonia in which the 3 atoms of hydrogen are displaced by 3 of mercury.

When white precipitate is boiled in water it is decomposed, and the heavy insoluble canary-yellow chloride of mercuramine is formed, whilst chloride of ammonium is formed in the solution; $2\ (Hg_2H_2NCl) + 2\ HO = (Hg_4H_2NO_2,Cl) + H_4NCl$. This yellow powder is dissolved easily by diluted nitric or hydrochloric acid.

If a solution of corrosive sublimate be added gradually to a boiling solution of sal ammoniac and free ammonia so long as the precipitate is redissolved by agitation, a compound crystallizes in rhombohedra on cooling; and the same substance is procured on boiling ordinary white precipitate in a solution of sal ammoniac. This compound fuses and undergoes decomposition at a temperature of 572°; boiling water extracts a large proportion of sal ammoniac from it, and leaves the canary-yellow powder above described. It is freely soluble in acids, even in acetic acid. Kane's analysis

of this compound would allow of its being represented by the formula HgH_3N,Cl. It is sometimes called *fusible white precipitate.*

When corrosive sublimate is exposed to a current of dry ammoniacal gas, it fuses with extrication of heat; 2 equivalents of the salt absorb 1 equivalent of ammonia, producing $H_3N, 2\,HgCl$. This compound may be sublimed without change, but it is decomposed by water: it is a true ammoniated chloride of mercury.

The following are the compounds which are produced by the combined action of ammonia and heat upon corrosive sublimate:—

(1) White precipitate	Hg_2H_2NCl.
(2) Red crystalline compound . .	$2\,HgCl,Hg_3N$.
(3) Chloride of mercuramine . .	$(Hg_4H_2NO_2)\,Cl$.
(4) Terchloride of mercuramine .	$(Hg_4H_2NCl_2)\,Cl$.
(5) Fusible white precipitate . .	HgH_3NCl.
(6) Ammoniated chloride of mercury	$2\,HgCl,H_3N$.

Besides the double salts, of which one is—

(7) Sal alembroth	$3\,H_4NCl,HgCl+Aq$.
(8) And another is	$H_4NCl, 2\,HgCl$.

These remarkable compounds derive interest from their connexion with the theories which have been proposed respecting the nature of ammonia, the consideration of which will be resumed when the alkaloids or organic bases are examined.

Two Bromides, analogous to the chlorides of mercury may be formed; they yield corresponding double salts; both of them may be sublimed without experiencing decomposition. The subbromide is white and insoluble. The bromide is crystallizable and soluble.

(782) Iodides of Mercury.—Mercury forms three iodides: a green subiodide, Hg_2I; a red iodide, HgI; and an intermediate iodide (Hg_2I,HgI) of a yellow colour, obtained by precipitating subnitrate of mercury by means of iodide of potassium containing iodine in solution.

The *subiodide* ($Hg_2I=327$) is a green powder insoluble in water, which is easily decomposed by exposure to light into mercury and the red iodide; the same change is effected by heating it gently with solutions of the soluble iodides or chlorides, or with hydriodic or hydrochloric acid. If heated suddenly it fuses and may be sublimed without decomposition; but if the temperature be raised gradually, it is decomposed into the red iodide and metallic mercury. It is easily formed by triturating 5 parts of iodine with 8 of mercury, moistening the mixture with a little alcohol; or it may be precipitated from a solution of any of the

salts of the suboxide of mercury, by adding to them a solution of iodide of potassium.

Iodide of Mercury ($HgI=227$; *Sp. Gr. of solid, 6·25; of vapour,* 15·68).—This beautiful compound may be obtained by triturating 5 parts of iodine with 4 of mercury, and subliming the mixture; but it is procured most easily by precipitating a solution of corrosive sublimate by means of a solution of iodide of potassium: the precipitate is soluble in an excess of either salt. The precipitate is at first salmon coloured, but it speedily becomes converted into a brilliant scarlet crystalline deposit. It fuses at about 400°, and yields a vapour of extraordinary density: as it cools it is deposited in yellow rhombic tables; this yellow colour is changed to red by mere agitation, or by scratching the crystals. Warington has shown that this change of colour depends upon a change in the molecular constitution of the salt, in consequence of which the rhomboidal crystals are converted into octohedra with a square base. Iodide of mercury is nearly insoluble in water, but it is taken up freely by alcohol. With the soluble electro-positive iodides it forms crystalline double salts, and it is dissolved easily by solutions of chlorides of the metals of the alkalies, but it does not form crystallizable compounds with these chlorides. A fusible double chloride and iodide of mercury ($HgI,HgCl$), may be formed; and a soluble crystallizable compound ($HgI, 2\,HgCl$), may be obtained by saturating a boiling solution of corrosive sublimate with the red iodide of mercury, and allowing it to crystallize. By adding a mixture of potash and ammonia to a solution of iodide of mercury in one of iodide of potassium, a brown powder is deposited, to which Nessler assigns the formula $Hg_4NI+2\,HO$. Iodide of mercury also forms definite compounds with the oxide, and with the sulphide of the metal.

(783) *Nitride of Mercury.*—Plantamour states, that by transmitting a current of dry ammoniacal gas over the yellow oxide of mercury precipitated from its salts by an alkali, and well dried at a temperature not exceeding 300°, water is formed and volatilized, whilst an anhydrous powder of a flea-brown colour is produced. It detonates powerfully when heated, or struck: the acids decompose it, forming salts of ammonia and mercury. Its probable composition is Hg_3N, as inferred from the mode of preparing it; $3\,HgO+H_3N=Hg_3N+3\,HO$.

(784) *Sulphate of Mercury; Mercuric Sulphate* ($HgO,SO_3=148$; *Sp. Gr.* 4·666).—When 2 parts of mercury are heated gently with 3 of oil of vitriol, sulphurous acid is evolved, and subsulphate of mercury is procured; but if the heat be increased, and the dis-

tillation be carried to dryness, the sulphate is formed; sulphurous acid being extricated, whilst the mercury takes oxygen from the sulphuric acid; $Hg + 2\,(HO,SO_3) = HgO,SO_3 + SO_2 + 2\,HO$. It is a white crystalline powder, which is soluble in a solution of common salt, but is decomposed by pure water into an insoluble yellow subsalt, called *turpeth mineral*, $3\,HgO,SO_3$, and a soluble supersalt, which crystallizes in deliquescent needles; the yellow subsalt is formed more rapidly if the sulphate be washed with boiling water. The normal sulphate, when treated with an excess of ammonia, yields sulphate of mercuramine. The normal sulphate unites with sulphate of ammonia, and forms a crystallizable double salt.

(785) NITRATES OF MERCURY.—Mercury forms a larger number of nitrates than any other metal. The conditions of temperature, and dilution of acid necessary to ensure the production of each compound, often vary in each case but little, and their accurate analysis is attended with some difficulty. Different chemists vary somewhat in their statements of the results which they obtained. The *normal subnitrate*, or *mercurous nitrate* ($Hg_2O,NO_5 + 2\,Aq$) is obtained by digesting metallic mercury in an excess of nitric acid diluted with 4 or 5 times its bulk of water: it crystallizes in short transparent somewhat efflorescent prisms (or in rhombic plates; Gerhardt); water decomposes it into a yellow insoluble dibasic salt ($2\,Hg_2O,NO_5 + HO$) and a soluble acid one. A soluble subnitrate, which is often mistaken for the normal salt, crystallizes in large transparent colourless prisms ($4\,Hg_2O,3NO_5 + HO$), and is obtained by digesting an excess of mercury in diluted nitric acid. De Marignac finds that by boiling the mother-liquors of the preceding salts upon an excess of mercury for several hours, doubly oblique, rhombic, colourless prisms are deposited, to which he assigns the formula, $5\,Hg_2O, 3\,NO_5, 2\,HO$. Other subnitrates also appear to exist. These various basic nitrates may be distinguished from the normal salt by triturating them with chloride of sodium, when they become grey, owing to the separation of suboxide of mercury, while calomel is formed; but the normal salt remains white.

A normal *nitrate of the red oxide*, $2\,(HgO,NO_5) + HO$, is slowly formed in voluminous crystals, by dissolving the red oxide of mercury in an excess of nitric acid, and evaporating the liquid until it assumes a syrupy consistence. Another nitrate ($2\,HgO, NO_5 + HO$) is deposited in acicular crystals from a boiling solution of mercury in excess of nitric acid; but it is obtained with greater certainty by saturating nitric acid, of sp. gr. 1·4, diluted with an equal bulk of water, with the red oxide of mercury. The

solutions of both these salts are decomposed when diluted freely with water, and a white insoluble basic nitrate ($3\ HgO,NO_5 + HO$) is precipitated: by long-continued washing with hot water, the whole of the nitric acid is removed from this basic salt, and oxide of mercury is left. Solutions of the nitrates of the red oxide of mercury, when digested upon an excess of the metal, are converted into nitrates of the suboxide.

(786) CHARACTERS OF THE SALTS OF MERCURY.—Most of the salts of mercury are colourless, but some of the basic salts of the red oxide are yellow. The following characters are common to the salts of both oxides. The soluble compounds have an acrid, nauseous, metallic taste: in large doses they act as irritant poisons. All the compounds of mercury are volatilized by heat. If a small quantity of any of the dry salts of this metal be placed at the bottom of a tube of the diameter of a quill, and be covered to the depth of an inch with a layer of dried carbonate of soda or of potash, mercury may be obtained in the form of a sublimate of minute globules, by heating the upper part of the layer of the carbonate to redness, and slowly driving the vapour of the mercurial compound over it.

The presence of mercury, when in solution, may be detected by placing a small strip of zinc, round which a thin slip of gold foil is twisted, in a portion of the liquid to be tested. The mercury will be deposited by voltaic action in the form of a white stain upon the gold. This stain will disappear on heating the gold to redness. The salts of mercury, whether soluble or insoluble, are all reduced to the metallic state when heated with a solution of *protochloride of tin*. A strip of metallic *copper* becomes coated with a white amalgam, if rubbed with a solution containing mercury. This test may be employed for detecting the presence of mercury in solution if applied by the method of Reinsch for arsenic (709), a sublimate of mercury in distinct globules being obtained by heating the coated slip in a small tube.

1.—*Salts of the suboxide* of mercury are characterized, when in solution, by yielding with solutions of *potash*, of *soda*, or of *lime*, a black precipitate of suboxide of mercury. *Ammonia* also gives a black precipitate. *Ferrocyanide of potassium* gives a white precipitate. Both *sulphuretted hydrogen* and *hydrosulphate of ammonia* yield a black sulphide of mercury. *Hydrochloric acid* and solutions of the *chlorides* cause a white precipitate of calomel, which is soluble in hot concentrated nitric acid, and in chlorine water; it is blackened by the addition of an excess of ammonia. *Iodide of*

potassium gives a green subiodide of mercury; and *chromate of potash* a bright red subchromate of the metal.

2.—*Salts of the red oxide*, when in solution, yield with solutions of *potash*, of *soda*, and of *lime*, a bright yellow precipitate of oxide of mercury; with *ammonia*, a white precipitate; with *normal carbonate of potash*, a yellow precipitate of oxide; with *bicarbonate of potash*, a red precipitate of oxychloride of mercury (780). *Hydrosulphate of ammonia* gives a black precipitate; and *sulphuretted hydrogen*, a dirty white precipitate, which passes through red into black. *Iodide of potassium* precipitates a salmon coloured iodide of mercury, which quickly becomes of a brilliant scarlet: this precipitate is soluble in excess both of iodide of potassium, and of corrosive sublimate. *Hydrochloric acid* and solutions of the *chlorides* give no precipitate with the salts of the red oxide of mercury. *Ferrocyanide of potassium* gives a white precipitate, which gradually becomes blue, while cyanide of mercury is formed in the solution.

(787) *Estimation of Mercury.*—Mercury is usually estimated in the metallic form. If the solution contain neither lead nor silver, metallic mercury may be precipitated by the addition of protochloride of tin, acidulated with hydrochloric acid: the metal must be collected on a weighed filter, and dried *in vacuo* over sulphuric acid.

When the compound is in the solid form, Millon recommends the following plan for effecting the decomposition of the combinations of mercury and for collecting the metal:—A hard glass tube, 15 or 16 inches long, such as is used in the analysis of organic

FIG. 337.

compounds, is drawn out in the manner represented in fig. 337, and at *a* a small bulb is formed for the reception of the mercury; a plug of asbestos is placed at *b*; the tube is then filled as far as

c with fragments of quicklime, and the mercurial compound in quantity varying from 15 to 50 grains is introduced between *c* and *d*, and the tube is filled up with fragments of lime. If nitric acid be present in the compound, metallic copper must be substituted for quicklime. The extremity, *e*, is connected with an apparatus, *g*, which supplies a steady current of pure dry hydrogen,—the tube being placed in a sheet-iron furnace, *f*, while the receiver, *a*, projects beyond the furnace, and is kept cool. As soon as the apparatus is filled with gas, lighted charcoal is applied to the first third of the tube between *b* and *c*, and when it is at a full red heat, glowing charcoal is very gradually added until the whole length of the tube is red hot; the mercury collects in *a*, and the water, which is at first condensed, is gradually removed by the current of dry hydrogen. When the operation is over, the narrow portion of the tube between *a* and *b* is cut with a file, and the detached portion *a*, with its contents, is weighed: the mercury is emptied, the bulb cleansed with nitric acid and water, then dried, and weighed a second time; the difference gives the weight of the condensed mercury.

§ II. Silver (Ag=108). *Sp. Gr.* 10·53.

(788) Silver has been known from the earliest ages, and has always been prized for its rarity, beauty, and its brilliant lustre. It has a white colour with a tinge of red; in hardness it is intermediate between copper and gold, and it is endowed with considerable tenacity; it may be hammered into very thin leaves, and admits of being drawn into very fine wire. By repeated heatings, however, this metal assumes a crystalline texture, and it then becomes brittle. It crystallizes in forms belonging to the regular system. Silver fuses at 1873° F., and on cooling expands forcibly at the moment of solidification. It is not sensibly volatilized if heated in closed vessels, but a silver wire is dispersed in greenish vapours when a very powerful electrical discharge is sent through it; when heated before the oxyhydrogen jet on lime (822) it may be made to boil, and give off vapours which become oxidized in the current of gas if it contains an excess of oxygen. Silver is an excellent conductor both of heat and electricity, and is not inferior in these respects to any known substance. Silver is not oxidized by exposure at any temperature either in a dry or a moist atmosphere. Pure silver, however, when melted, absorbs oxygen mechanically, to an extent amounting, it is said, to 22 times the bulk of the metal, but the gas is given off at the moment of solidification: if

a mass of melted silver be allowed to cool suddenly, the outer crust becomes solidified, and when the interior portion assumes the solid condition it ruptures the crust; small tubes or globules of melted metal are then forcibly expelled by the escaping oxygen, aided by the sudden expansion which the silver undergoes in the act of solidification. This phenomenon, which is termed the *spitting* of the globule, is entirely prevented by the presence of 1 or 2 per cent. of copper. Silver combines slowly with chlorine, with bromine, and with iodine: if fused with phosphorus the two bodies enter into combination. Silver has a powerful affinity for sulphur; by long exposure to the air the metal becomes superficially blackened or tarnished, from the formation of a thin film of sulphide upon its surface, owing to the decomposing action of the metal upon the small portion of sulphuretted hydrogen which is constantly floating in the air, especially of large towns. This tarnish is readily removed by means of a solution of cyanide of potassium.

The best solvent for silver is nitric acid, which, if diluted with an equal bulk of water, acts upon the metal with great violence, dissolving it rapidly and evolving binoxide of nitrogen, while nitrate of silver is formed. Hydrochloric acid acts but slightly upon it. Aqua regia attacks it more rapidly. Diluted hydriodic acid attacks it with evolution of hydrogen. Boiling oil of vitriol oxidizes it with evolution of sulphurous acid. If common salt be fused in a silver dish, or if it be moistened and left in contact with silver, it gradually corrodes it; soda being formed by the absorption of oxygen from the air, while the liberated chlorine attacks the silver. Neither the alkalies nor their nitrates exert any considerable action upon it, whether in solution or when fused by heat, and hence crucibles for the fusion of refractory minerals with caustic potash are commonly made of this metal.

The value of silver as a medium of exchange has caused it to be adopted as such by all civilized nations from the earliest ages of the world. When alloyed with certain proportions of copper it is used for the current coin of the realm, and for the various articles of plate. From its superior power of reflecting light, it forms the best surface for the reflectors employed in lighthouses at sea.

(789) *Extraction of Silver from its Ores.*—Silver is frequently met with in the native state; either pure, when it occurs in fibrous masses, or crystallized in cubes or octohedra, or sometimes combined with gold, mercury, or antimony: generally, however, it is found in combination with sulphur, mixed with sulphides of lead, antimony, copper, and iron. The mines of Peru and Mexico are

the most extensive sources of silver. In Europe, those of Kongsberg in Norway, and of Schneeberg and Freyberg in Saxony, are celebrated: there are also numerous other mines from which smaller quantities are obtained. The ores of silver occur usually among the primitive rocks, frequently in calcareous veins, traversing either gneiss, or slaty and micaceous deposits. Sulphide of lead is nearly always accompanied by small quantities of sulphide of silver, and a considerable quantity of silver is extracted during the refining of lead by Pattinson's process, as well as by cupellation.

At Freyberg, silver is for the most part obtained from the sulphide by the method of *amalgamation*. The plumbiferous ores are in this case rejected, as they are not adapted to this method of proceeding, but are treated in the manner already mentioned (753). The ores are usually sorted, so that they shall contain about 0·24 parts of silver in 100, or about 80 ounces per ton of ore, and not more than 1 per cent. of copper; the proportion of iron pyrites is not allowed to exceed, or greatly to fall short of 35 per cent. The metalliferous mass, after being reduced to a coarse powder, is mixed with a tenth of its weight of common salt, and sifted, to ensure its intimate incorporation: it is then roasted, at first at a low red heat; during this operation, care is taken to keep the mixture constantly stirred, in order as far as possible to prevent it from concreting into lumps. Meantime arsenic and antimony are expelled in dense white fumes of arsenious acid and oxide of antimony, and the sulphides of the other metals are partially oxidized: the silver obtains chlorine from the salt, the sodium of which unites with oxygen and sulphur, chloride of silver and sulphate of soda being formed; the copper and the iron are changed partly into sulphates, partly into chlorides, and partly into oxides, as the equations subjoined will show:—

$$AgS + NaCl + O_4 = AgCl + NaO,SO_3;$$
$$CuS + O_4 = CuO,SO_3;$$
$$2\ CuS + 2\ NaCl + 8\ O = Cu_2Cl + Cl + 2\ (NaO,SO_3);$$
$$2\ FeS_2 + 3\ NaCl + 14\ O = Fe_2Cl_3 + 3\ (NaO,SO_3) + SO_2.$$

During the early stages of this operation, fumes of sulphurous acid are given off abundantly, and the roasting is continued until these have in great measure given place to those of chlorine and perchloride of iron. A charge of $4\frac{1}{2}$ cwt. requires 6 hours' roasting. The roasted mass is now raked out of the furnace, and allowed to cool: it is next sifted in order to separate the lumps, which are powdered and again submitted to the same operation. About 85 per cent. of the silver is thus converted into chloride at the first

roasting. The portions which have passed through the sieve are ground to powder, and passed through a bolting sieve to procure a very fine meal. The powder is next placed, with from a third to half its weight of water, in large casks, which are charged with half a ton of the ore. These casks are caused to revolve upon horizontal axes, about 20 times per minute; 1 cwt. of scrap wrought iron is then introduced into each cask, and after the lapse of an hour, 5 cwt. of mercury is added, after which the casks are again made to revolve for about 20 hours; during this operation a slight rise of temperature is observed. The powder when placed in the casks consists principally of chloride of silver mixed with large quantities of sulphate and dichloride of copper, and of the sesquichloride of iron, with a variable proportion of the oxides of the two latter metals. The object of agitating the mixture with the iron before adding the mercury, is to reduce the sesquichloride of iron to protochloride in the first instance; if this precaution were not taken, the mercury would be partially converted into calomel, which would not subsequently be decomposed, and would thus be lost: the excess of iron afterwards removes the chlorine from the chloride of silver and dichloride of copper, and the sulphuric acid from the copper.

$$Fe + Fe_2Cl_3 = 3FeCl; \quad AgCl + Fe = FeCl + Ag.$$
$$Cu_2Cl + Fe = FeCl + 2\,Cu; \quad CuO,SO_3 + Fe = FeO,SO_3 + Cu.$$

The presence of the mercury favours this reaction, by establishing a voltaic current, and the silver and copper thus set at liberty unite immediately with the mercury, forming a liquid amalgam. At the expiration of 18 or 20 hours the casks are filled up with water, and are again set in motion for a couple of hours to allow the amalgam to be washed out of the spent materials; after which the fluid amalgam is drawn off into sacks of ticking; these sacks form a kind of rude filter, through which the greater part of the mercury runs into a stone trough, leaving behind it a soft solid containing from 15 to 17 per cent. of silver. The mud in the casks is again submitted to washing; the residual amalgam subsides, owing to its greater density, and the lighter portions are rejected. The filtered part of the mercury, which retains a small quantity of silver, is used again for the amalgamation of a fresh portion of ore. The silver in the solid amalgam has now to be separated from the remaining mercury; for this purpose it is placed in trays, supported on a tripod, C, fig. 338, under a large distillatory iron bell, B, round the upper part of which a fire, A, is lighted; the bell and its contents are thus brought to a red

heat, by which means the mercury is driven off; its vapour descends, and is condensed in the water contained in the vessel, D. The operation is generally performed on 5 cwt. of amalgam at a time, and occupies 8 hours. The residual spongy mass of silver and copper is then fused and cast into ingots, which in the Saxon mines consist usually of about 70 parts of pure silver and 28 of copper per cent.*

FIG. 338.

(790) *American Process of Amalgamation.*—In the mining districts of Mexico and Chili, where fuel is expensive, and where ores are often worked of a much poorer description than in Europe, the process of amalgamation is different. A good deal of the silver occurs in the native state, so that it unites directly with the mercury. The mineral is stamped and ground to a fine powder in mills, then moistened with water, and mingled with from 1 to 5 per cent. of salt; the mixing is effected by the trampling of horses during 6 or 8 hours. The ore thus blended with the salt is allowed to remain undisturbed for some days, after which an addition of $\frac{1}{200}$th or $\frac{1}{100}$th of its weight of what is technically termed *magistral*, is made. This substance consists of roasted copper

* An improvement upon this process has been introduced by Augustin, who dispenses with the use of mercury altogether. After the ore has been roasted first by itself, and again a second time with chloride of sodium, it is digested in a concentrated solution of common salt;—such a solution dissolves chloride of silver readily: a dilute solution of chloride of sodium exerts little or no solvent action; and the concentrated liquid when diluted deposits the chloride of silver which it had previously dissolved. In practice it is found better, instead of diluting the liquid, to digest it upon metallic copper; the chloride of silver is decomposed, chloride of copper is formed and dissolved, whilst metallic silver is precipitated. The presence of chloride of copper in the solution of the chloride of sodium does not prevent the liquid from being employed again for the extraction of chloride of silver from fresh portions of the roasted ore.

Another important improvement in the operation was made by Ziervogel. He avoids the preparation of chloride of silver entirely, and merely roasts the sulphurous ores in such a manner that the sulphates of iron and copper are completely decomposed, whilst the sulphate of silver, which withstands a much higher temperature, remains undecomposed in the mass. In this operation the powdered ore is roasted till it gives off no odour of sulphurous acid, and yields no sensible amount of sulphate of copper when thrown red hot into water: boiling water then dissolves out the sulphate of silver, but the oxides of copper and iron remain undissolved. The silver is precipitated from the liquid by means of metallic copper as before. A small quantity of silver is still retained in the undissolved residue, from which it may be advantageously extracted by the method of Augustin. Both these processes have been patented and practised on a large scale in England.

pyrites, and contains about 10 per cent. of sulphate of copper, the remainder being sulphate of iron and other impurities; mercury, to the extent of twice the quantity of silver that the ore contains, is then added, the mixture being effected, as before, by the trampling of horses. It is again allowed to rest for 16 or 20 days: during this period a considerable portion of the silver becomes united with the mercury, forming a hard, brilliant amalgam, and at the same time a large quantity of calomel is formed. Another equal quantity of mercury is added, and a still longer interval of rest is allowed; then a third dose of mercury to the same extent follows; by this last addition a fluid amalgam is obtained, which is separated by washing, filtered, and the mercury is expelled from the silver by distillation. The quantity of mercury consumed in this process varies from 130 to 150 parts for each 100 parts of silver extracted, great waste being incurred owing to the formation of calomel, which is not recovered. It is calculated that up to the close of the last century, 6 million cwt. of mercury had thus been lost by the processes adopted in the American mines in the course of 200 years.*

The theory of this operation is rather obscure. The sulphate of copper of the magistral, and the chloride of sodium decompose each other, chloride of copper and sulphate of soda being formed. Chloride of copper, in the presence of metallic silver, is converted into dichloride of copper, whilst chloride of silver is produced; $2\,CuCl + Ag = Cu_2Cl + AgCl$. When dichloride of copper, with excess of common salt and water, is brought into contact with sulphide of silver, the dichloride of copper is dissolved by the solution of chloride of sodium; the dichloride of copper, when in solution, decomposes the sulphide of silver, and is converted into disulphide, whilst chloride of silver is formed; $Cu_2Cl + AgS = Cu_2S + AgCl$. The excess of salt dissolves the chloride of silver, and the addition of mercury decomposes this dissolved chloride; calomel is formed, and an amalgam of silver is procured; $AgCl + 2\,Hg = Hg_2Cl + Ag$. If too much magistral be added, an excess of chloride of copper ($CuCl$) is produced; this state of the mixture is easily perceived, as in such a case the globules of mercury in the mixture appear to be too minutely divided; the addition of lime then becomes neces-

* Dumas proposes to recover this mercury by treating the washed residue with a quantity of chloride of lime or nitrate of soda, proportioned to the mercury they contain, then adding hydrochloric acid in slight excess; the calomel would thus be converted into corrosive sublimate. This is to be removed by methodical washing, and the mercury precipitated by copper. The solution of copper thus obtained would furnish the magistral required for a new operation upon fresh ore.

sary in order to decompose the excess of the chloride of copper, otherwise this salt would reconvert the silver into chloride, and the mercury into calomel.

(791) *Separation of Silver from Copper by Liquation.*—It occasionally happens that a copper ore contains a considerable amount of silver, which, under certain circumstances, it may be desirable to extract by the process of *liquation*. For this purpose the copper, having been brought to the stage of blister copper (733), is melted with from 3 to 4 times its weight of lead: the mixture is cast into circular ingots in iron moulds, which suddenly cool the alloy, and cause it to solidify before the copper and lead have time to separate from each other. The proportion of lead should not be less than 500 times that of the silver in the mass. These cakes are then subjected to the action of a moderate heat; the lead, combined with nearly all the silver, and a small proportion of copper, gradually runs from the mass, leaving a spongy residue, consisting chiefly of copper, but still retaining a small proportion of lead. The argentiferous lead is afterwards subjected to the process of cupellation (753), whilst the copper from which it has been separated is subjected to a patient roasting in order to oxidize the remainder of the lead, and is then refined much in the usual manner.

(792) *Plating and Silvering.*—Silver is frequently employed to give a coating to the surface of less expensive metals. Goods so prepared are said to be *plated*, if the proportion of silver be considerable, and *silvered* if it be small. Plating on copper is effected by polishing the upper surface of the ingot which is to be plated, and then placing upon it a bright slip of silver, the superficial area of which is a little smaller than that of the copper which it is intended to cover: the thickness of the plate of silver in proportion to that of the copper varies with the value of the goods. The compound ingot is then exposed to a temperature just below the fusing point of the silver, which softens at its surface. By hammering or rolling out at this high heat, the two metals are *sweated* together, as it is termed, and become inseparably united. No solder is used in this process, but a small portion of powdered borax is placed round the edge of the silver to prevent the surface of the copper from becoming oxidated. The ingot is then rolled until it is reduced to the required degree of tenuity.

Plating on steel is effected rather differently. The article (a dessert knife, for example), having been first brought to the shape required, is tinned upon its surface, and then a slip of silver foil is soldered on. After the silver has been attached, the super-

fluous portion is removed, and the article is finished up and polished.

These methods of plating have, however, been in a great degree superseded by the process of electro-plating, in which the silver is deposited upon the surface by voltaic action. The mode of doing this will be explained hereafter (877).

Silvering may be effected either by the *wet* or by the *dry* method. The wet method is usually adopted for such purposes as the silvering of thermometer scales. It is generally executed either on brass or copper: the surface of these metals is cleaned by *dipping*, or momentary immersion of the articles in nitric acid, to remove the film of oxide which always forms from exposure to the atmosphere, even for a few hours. They are then rubbed over with a mixture of 100 parts of cream of tartar, 10 of chloride of silver, and 1 part of corrosive sublimate. The mercury appears to act as a kind of solder to the silver, the copper combining with the chlorine both of the chloride of silver and of the sublimate; the surface is afterwards polished.

Dry silvering is effected by dissolving a certain quantity of silver in mercury; the 'dipped' articles are agitated with a portion of this amalgam, which thus becomes diffused uniformly over the surface. By the application of heat the mercury is expelled, leaving a very thin film of silver behind: on polishing the trinkets a bright silvered surface is obtained.

(793) *Silvering of Mirrors.*—Some of the salts of silver when rendered slightly ammoniacal and mixed with certain organic solutions, such as aldehyd and salicylous acid, are reduced to the metallic state, the silver being deposited upon the surfaces of glass vessels in which the experiment is made, in the form of a brilliant, adhering, mirror-like coating. Mr. Drayton some years ago proposed to apply this observation to the silvering of mirrors upon the large scale, as the coating adapts itself not only to flat surfaces, but to those also which are curved, or cut into patterns. This process is now successfully practised at Paris, as follows:—600 grains of pure neutral nitrate of silver are dissolved in 1200 grains of water. To this solution are added: 1st, 75 grains of a liquor prepared from 25 parts of distilled water, 10 of sesquicarbonate of ammonia, and 10 of a solution of ammonia of sp. gr. 0·980; 2nd, 30 grains of a solution of ammonia of sp. gr. 0·980; and 3rd, 1800 grains of alcohol of sp. gr. 0·850. The mixture is left at rest to become clear. The liquid is decanted or filtered, and a mixture of equal parts of alcohol (sp. gr. 0·850) and oil of cassia is added in the proportion of 1 part of this *essence of cassia*

to 15 parts of the solution of silver; the mixture is agitated and left to settle for several hours, after which it is filtered. Just before pouring it upon the glass to be silvered, it is mixed with $\frac{1}{78}$th of its bulk of *essence of cloves* (composed of 1 part of oil of cloves, and 3 of alcohol, sp. gr. 0·850). The glass, having been thoroughly cleansed, is covered with the silvering liquid, and warmed to about 100° F., at which temperature it is maintained for two or three hours: the liquid is then decanted, and may be employed for silvering other glasses. The deposit of silver upon the glass is washed, dried, and then varnished. (Pelouze and Fremy, *Traité de Chimie*, 2nd Ed., iii. 347.)

An alcoholic solution of grape sugar produces the same result, if substituted for the oils of cassia and cloves, but the deposit occurs much more slowly. Liebig's method of reducing an ammoniacal solution of nitrate of silver alkalized with soda or potash, by means of milk sugar, at ordinary temperatures, has been successfully applied by Steinheil, in the following manner, to the silvering of mirrors for telescopes (*Liebig's Annal.*, xcviii. 132):—Dissolve in 200 measures of water $\frac{1}{20}$th of their weight of pure nitrate of silver, and add to the liquid a solution of caustic ammonia in quantity just sufficient to redissolve the oxide of silver which is at first precipitated; add to this solution 450 measures of a solution of caustic soda (of sp. gr. 1·035) free from chloride, and immediately redissolve the dark brown precipitate thus produced by the cautious addition of caustic ammonia, after which dilute the liquid with water to 1450 measures; then add a solution of nitrate of silver till a decided permanent grey precipitate is formed, and finally pour in water till the mixture occupies exactly 1500 measures: then leave it to stand, and decant the clear liquid. Immediately before the solution is to be used, it is to be mixed with $\frac{1}{8}$th or $\frac{1}{10}$th of its volume of a solution of milk sugar in ten times its weight of water. The solution is to be placed in a shallow vessel, and the glass to be silvered supported just at the surface of the liquid: a beautiful coherent film of silver is deposited upon the under surface of the glass, and a copious precipitation of silver occurs upon the sides of the vessel.

Another very good method of silvering glass is that of Petit Jean (*Chem. Gaz.*, 1856, p. 319), in which an ammoniacal solution of tartrate of silver is employed at a gentle heat; by using an ammonio-citrate of gold in solution, it is easy to gild upon glass; and in a similar manner the surface may be platinized if a solution of platino-tartrate of soda be employed.

(794) *Alloys of Silver.*—Various alloys of silver may be obtained with facility, but the only one extensively used is the alloy

of silver with copper. Pure silver is too soft for ordinary uses, such as the fabrication of coin and jeweller's work, and would soon waste by the constant friction it would experience. In order to confer a sufficient degree of hardness upon the silver, it is combined with a small portion of copper. The proportion of copper in the 'standard' silver employed for coinage varies in different countries: in England it amounts to 7·5 per cent., in France to 10 per cent., and in Prussia to 25 per cent. Silver and copper in uniting to form an alloy expand slightly, so that the density of the mixture is somewhat less than the calculated mean. English standard silver has a density of 10·20, instead of 10·35. Experience has shown that an alloy of silver and copper, however carefully the two metals be incorporated, undergoes a species of liquation during the slow solidification of the melted mass; when cast into ingots, the interior parts of the bars have a composition different from that of the superficial portions: a circumstance of some importance in the preparation of standard silver for the purposes of coinage. The only alloy in which this partial separation of the two metals was found not to occur is stated by Levol (*Ann. de Chimie,* III. xxxvi. 220), to consist of 719 parts of silver and 281 of copper, corresponding to the formula Ag_3Cu_4. This liquation is comparatively trifling in amount in bars which contain 950 parts of silver and upwards in 1000: in bars which contain a larger proportion of silver than 719 in 1000 of alloy, the central portions of the ingot were found to be richer than those upon the surface; but in the alloys of lower value the proportion of silver was greatest on the surface of the ingot. Many of the metals when alloyed with silver in small quantity render it brittle and unfit for the purposes of coinage. This is the case, for instance, when the silver contains tin, zinc, antimony, bismuth, lead, or arsenic. These metals are, however, all easily removed in the ordinary course of refining. The alloy used as a *solder* for silver consists of 6 parts of brass, 5 of silver, and 2 of zinc. Silver appears to have the power of dissolving its sulphide: a quantity of sulphide not exceeding 1 per cent. renders the mass so brittle that it cannot be rolled.

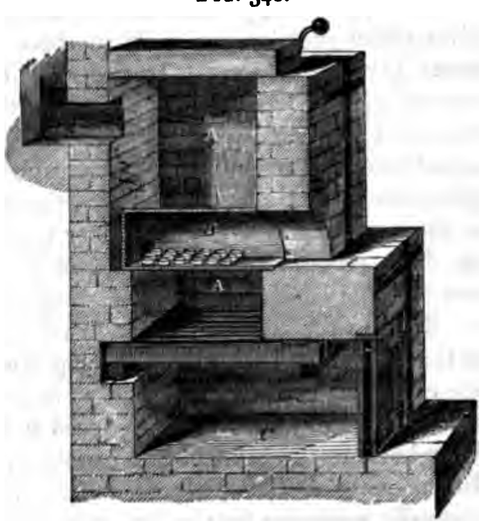
(795) *Assay of Silver by Cupellation.*—From the high price of silver, compared with that of the metals used to harden it, it has become an object of great importance to be able to determine with facility and with accuracy the proportion of silver in any compound. Jeweller's silver must according to law be of a certain degree of fineness. In this country each article, previous to being sold, is tested at Goldsmiths' Hall, and if approved is stamped. The

method of testing commonly employed is termed *assaying* or *cupellation.* In principle it depends upon the property which lead possesses of absorbing oxygen at a high temperature, and of forming with it an easily fusible oxide, which imparts oxygen with facility to all those metals which yield oxides not reducible by heat alone. Most of the oxides* thus formed unite with the oxide of lead, and produce a fusible glass which is easily absorbed by a porous crucible made of burnt bones, termed a *cupel;* whilst any silver that the mixture contains is left behind in a bright globule, which admits of being accurately weighed. The cupel and its contents are shown in section in fig. 339. These cupels are prepared from bone ash (burnt to whiteness, and ground to a fine powder), by moistening it with water: a suitable quantity of the mixture is placed in a mould, and the required form and coherence is given to it by the blow of a mallet or of a press: the cupels are allowed to dry thoroughly before they are used. The assay may be conducted upon quantities of silver varying from 10 to 20 grains in weight.

FIG. 339.

The plan of proceeding is as follows:—In a convenient furnace, such as is shown in section at A A, fig. 340, is placed an earthenware oven or muffle, B, of semicylindrical form, closed at one end, and open at the other, with slits in the sides to allow the free circulation of the air; upon the floor of the muffle, a number of cupels are arranged in rows, and the temperature is raised to bright redness. Equal portions of the various samples of silver to be assayed are in the meantime accurately weighed, and wrapped in a quantity of pure thin sheet-lead, the weight of which varies with the purity of the alloy; the larger the proportion of foreign metals

FIG. 340.



* Oxides of tin, zinc, nickel, and iron do not form a fusible combination with litharge, and the alloys which these metals form with silver are consequently not adapted for cupellation.

that it contains, the greater is the quantity of lead needed. Each piece for assay is now placed in its allotted cupel, by means of a long pair of tongs. It quickly fuses; fumes of oxide of lead are seen rising from the cupels, but the greater part of the oxide is absorbed by the cupel, and the silver is left behind in a state of purity. At the moment that the last portion of lead undergoes oxidation, the surface of the silver flashes, or lightens, as it is technically termed, owing to the cause already explained (753). This phenomenon indicates that the process is completed. The button is allowed to cool very gradually, to prevent the loss of silver by dispersion from *spitting* (788); it is then detached from the cupel, brushed, and accurately weighed. If the piece of alloy originally taken weighed 10 grains, the weight of the button in hundredths of a grain gives the number of parts of silver in 1000 parts of alloy. A minute quantity of silver always passes into the cupel during the process, for which an allowance must be made in weighing the button; and if the proportion of lead be too great this loss is increased, but if too little be used, part of the copper is left in the bead. Upon an alloy which contains 925 parts of silver to 75 of copper, the loss is about 4 per 1000; and upon silver which contains 900 parts in 1000, the loss on the button is about 5 parts in 1000. In order to be able to estimate the amount of this loss in each operation, the best plan is to pass three or four *proofs*, with each set of assays. These proofs consist of pieces of fine silver of known weight, which are mixed with quantities of lead and copper, approximately of the same amount as those present in the assays under trial. The loss experienced by these proofs affords a method of checking the results of the assay. The amount of this loss varies with the temperature.

The most convenient system of reporting the fineness of silver is the decimal method, which is employed in most countries with the exception of England. The practice of reporting both gold and silver decimally was introduced a few years ago by Sir J. Herschel into the Mint of this country, and it probably will gradually supersede the cumbrous and artificial method which is still generally employed by the English assayers. Upon the decimal system, fine silver is termed 1000·0, and the report upon any sample of alloy simply indicates the number of parts of pure silver in 1000 which it contains. Thus English standard silver contains 925 parts of silver, and 75 of copper in 1000 of the alloy. French standard contains 900 parts of silver, and 100 of copper in 1000 of alloy. English standard would therefore be reported as 925; French standard as 900.

The proportions of lead which are generally employed for the cupellation of different alloys are the following:—

If 1000 parts of the alloy contain	It will require of lead
1000 parts of fine silver . . .	half its weight.
950 „ . . .	3 times its weight.
925 „ . . .	$5\frac{1}{2}$ „
900 „ . . .	7 „
850 „ . . .	9 „
800 „ . . .	10 „
700 „ . . .	12 „
600 „ . . .	14 „
500, or less „ . . .	16 or 17 „

A skilful assayer will generally be able at once to determine the comparative fineness of an article from its mere appearance, and will judge accordingly of the proportion of lead which it will require. Great care is needful in regulating the temperature of the furnace during the cupellation: if too high, a part of the silver will be lost by volatilization; if too low, portions of lead and copper are liable to be retained. When the assay is properly performed, the button is brilliant, well rounded, free from irregularities, and somewhat granular upon its surface: it is readily detached from the cupel. If the assay adheres strongly to the cupel, or is irregular in its outline, it retains a portion of alloy.

(796) *Assay of Silver by the Humid Process.*—The results of the process of the assay by cupellation, even in experienced hands, may vary as much as 2 parts in 1000: this circumstance induced Gay-Lussac to contrive a different method, which is now adopted not only in the French Mint, but is employed in the Mints of Great Britain and the United States, as well as in almost all the Mints of Europe; it admits of an accurate estimate of the value of an alloy to within 0·5 in 1000. This process depends upon the precipitation of the silver in the form of an insoluble chloride, and the measurement of the amount of a standard solution of chloride of sodium which is required to effect the complete precipitation of the silver in a given weight of the alloy. Chloride of silver easily collects into dense flocculi by agitation in a solution which is acidulated with nitric acid, and which contains no excess of soluble chlorides; so that the exact point at which the precipitate ceases to be formed is readily perceived.

A solution of common salt is prepared of such a strength that 1000 grains of it are exactly sufficient to precipitate 10 grains of pure silver. 10 grains of the alloy for examination are placed in

a stoppered bottle, capable of holding about 6 oz. of water, and by the aid of a gentle heat are dissolved in 2 drachms of nitric acid, of specific gravity 1·25: the solution of salt is then placed in a burette (fig. 341) capable of holding rather more than 1000 grains. The burette, when filled with the solution, is weighed before being used, and the liquid is added to the nitrate of silver in the bottle; when it is supposed that the silver is nearly all precipitated, the liquor is briskly agitated in the bottle, and the precipitate is allowed to subside; a drop or two more of the solution of salt is then added: if a precipitate be produced, the liquid is again agitated; and when clear, more of the solution is added, as before, so long as any turbidity is produced by the addition. When a cloud ceases to be formed, the proportion of solution of salt which has been added is ascertained by weighing the burette a second time. The number of grains of the solution employed indicates the degree of fineness of the alloy.*

FIG. 341.

When, as in the assay of bars for coin, or for jeweller's work, a large number of assays must be executed, all very nearly of uniform fineness, the operation may be reduced to a system by which its precision may be increased, at the same time that it is rendered much more easy of execution. For this purpose, two solutions of salt are employed: one, the *standard solution*, containing in 1000 grains a sufficient quantity of commercial chloride of sodium to precipitate 10 grains of silver†; the second solution, the *decimal solution*, having one tenth of the strength of the first, and being prepared by diluting 1 pint of the standard solution with 9 pints of water. These solutions are to be preserved in well-closed bottles. The standard solution is prepared in large quantities at a time, and kept in stoneware jars, A, fig. 342, capable of containing 20 or 25 gallons: *b* is a tube open at both ends, which passes nearly to the bottom of the jar, to admit air, whilst the liquid is

* In the Calcutta Mint this precipitate is washed by subsidence in the vessel in which it is formed, and is then collected in a small porcelain crucible, as in the process of collecting gold, in the operation of *parting* (814). The chloride is dried, and then weighed, and the corresponding value of the silver is calculated.

† This solution contains approximately 380 grains of chloride of sodium in a gallon: but, as the commercial salt contains chloride of magnesium, the exact strength must be determined by dissolving 10 grains of fine silver in acid, and precipitating it by the addition of 1000 grains of the solution, ascertaining the amount of the excess or deficiency of chloride in the manner about to be detailed, and then adding water or salt as may be needed.

drawn off by the stop-cock, *c*, without allowing any loss by evaporation; *d* is a gauge by which the quantity of liquid within is indicated. A series of bottles, capable of containing about 6 fluid ounces each, is fitted with ground stoppers, numbered consecutively from 1 upwards: into each bottle 10 grains of the alloy for assay is weighed; 2 drachms of nitric acid are added to each bottle, which is placed in a shallow vessel containing water, and gradually raised to the boiling point; in ten minutes the alloy is completely dissolved.

FIG. 342.

The precipitation of the silver in the form of chloride is then effected by the aid of the apparatus now to be described:—*g*, fig. 342, is a glass pipette which can be filled with the standard solution. The quantity of liquid introduced into the pipette is regulated by means of the stopcock, *e f*, the peculiar construction of which is shown on a larger scale in fig. 343, in which *e* represents an ordinary stopcock (constructed of silver to resist the action of the solution), terminating below in a long tube, *c*; at *f* is an opening for the escape of air, which can be closed at pleasure by the plug, *a*. Suppose it be desired to fill the pipette, *g*, fig. 342; the lower opening of the pipette is closed by the fore-finger, the solution is admitted by opening the stop-cock, *e*, whilst the air escapes at *f*, which is open; as soon as the liquid has risen a little above the mark, *n*, both the stop-cock, *e*, and the plug at *f* are closed, and the finger is withdrawn. In this position the pipette

will retain its charge for an indefinite time. The apparatus represented at *m l* is intended to facilitate the exact emptying of the pipette; the tray, *h i*, slides easily between two grooves, in which its motion is limited by the stops, *l* and *m*; *h* is a compartment for the reception of the assay bottles, so adjusted that when the tray rests against the stop, *m*, the pipette shall empty itself into the bottle without wetting its neck; *i* is another compartment for receiving the superfluous solution of salt, and *k* represents a piece of sponge, the object of which is to remove the drop which hangs to the lower end of the pipette; the stop, *l*, is so placed, that when the slide rests against it, the sponge shall just touch the lower extremity of the pipette. The sponge, *k*, having been brought to touch the lower end of the pipette, the plug at *f* is slightly relaxed to allow the air to enter, and a portion of the liquid gradually to escape, until it has fallen exactly to the mark, *n*. The slide is now moved until the bottle, *h*, is directly underneath the pipette, and on opening the plug at *f* to its full extent, the charge flows freely into the bottle.

FIG. 343.

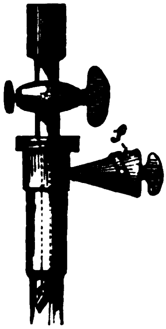
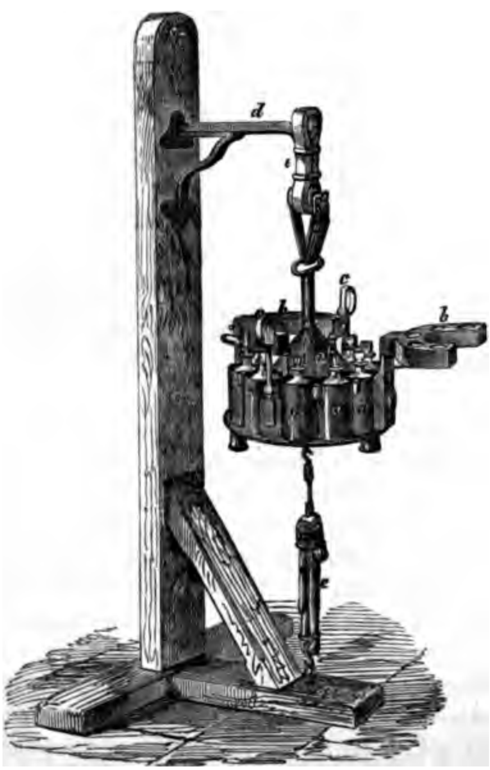


FIG. 344.



Suppose now the object of the assay be to ascertain whether a certain number of bars be of the fineness of English standard silver, or if not, what is the amount of their variation from standard. The pipette, *g*, is so graduated that when filled up to the mark, *n*, it shall deliver exactly 922 grains of the standard solution, which will contain a sufficient

amount of common salt to precipitate 9·22 grains of silver; a quantity which is purposely rather less than the assay is expected to contain; 10 grains of alloy, if of correct composition, containing 9·25 grains of silver. When each bottle in succession has received from the pipette a charge of exactly the same value, the bottles are transferred to the *agitator*, shown at fig. 344, which is suspended from an iron arm, *d*, between two strong springs, *e*, *e*, made of vulcanized caoutchouc. This agitator is usually constructed to contain 10 bottles, which are lodged in the compartments, *a*, *a*; the stoppers are secured in their places by the rims, *b*, *b*, one of which is represented in the figure as thrown back for the admission of the bottles; the rims when closed are confined by the springs shown at *c*, *c*. On agitating the apparatus briskly for 60 or 80 seconds, the solutions become clear, and the bottles are removed from the agitator, and transferred to a stand, behind which is a blackboard divided into 10 numbered compartments, each bottle being placed opposite the compartment which corresponds with its number.

The adjustment of the remaining portion of the assay is made by means of the *decimal solution*. This is contained in a small bottle of 10 or 12 ounces in capacity, fig. 345, provided with a tube or small pipette, *b*, open at both ends, but drawn out to a narrow aperture below. On this small pipette a mark, *c*, is made at a height corresponding exactly to 10 grains of the liquid; 10 grains of this solution containing sufficient chlorine to precipitate 0·01 grain of silver.

Fig. 345.

The assayer now plunges this small pipette into the decimal solution, and closing the upper opening of the tube with his forefinger, partially withdraws it from the bottle, and allows the liquid to escape until it stands exactly at the line of the graduation, *c*; he then transfers the pipette to the first bottle, and allows the solution to flow into it. The same operation is repeated with each assay bottle in succession. A mark is next made with a piece of chalk, opposite to each bottle in which a precipitate is occasioned. These bottles are then replaced in the agitator, and shaken a second time; the solutions having thus again been rendered clear, are replaced upon the table, and a second pipette of the decimal solution is added to each of the bottles in which a precipitate was first produced. This operation is repeated until in each bottle no

further precipitate is occasioned. The contents of the pipette, *g*, of the standard solution, which have been added to each assay, occasion a precipitate out of the 10 grains equal to 9·22 or of 922 parts out of 1000 parts of alloy. Each pipette of decimal solution is equivalent to $\frac{1}{1000}$ th of fine silver in the alloy, and by counting the number of marks against each bottle, reckoning the last only as equal to $\frac{1}{2}$, since a portion of it probably remains in the liquid in excess, the assayer ascertains the value of each bar. If, for instance, two marks stand opposite to any bottle, the fineness of the bar will be more than 923, but less than 924, and may be reported as 923·5.

If, however, there be any bottles in which the addition of the first pipette of the decimal solution produces no precipitate, these samples must be either exactly of the fineness 922, or below that point. The following method is adopted for completing the assay of these samples: a *decimal solution of silver* is prepared by dissolving 10 grains of pure silver in nitric acid, and diluting it with distilled water till the solution occupies the bulk of 10,000 grain-measures of water; each 10 grains of this liquid will then contain exactly 0·01 grain of silver. A bottle of this solution is provided with a pipette similar to that shown in fig. 345, but graduated to deliver 50 grains of the liquid from the mark, *d*. Each of the assay bottles, which indicates a fineness below 922, is supplied with 50 grains of this decimal silver solution, or with 0·05 grain of silver; a mark of -5 is made upon the board against each of these bottles. The bottles are then agitated as before, and a fresh dose of 10 grains of the decimal *salt* solution is now added to each; if a cloud be thus produced, a mark is chalked against each bottle in which a precipitate is observed, and the bottles are again agitated, and another dose of decimal salt liquid is added, and so on, until a precipitate ceases to be formed. Suppose that the first two pipettes of the solution produce a cloud, but the third does not; each bottle, it will be remembered, received a dose of salt solution in the first instance, as usual, in addition to the quantity received after the decimal silver solution was added; the quantity of salt which has produced a precipitate is therefore equivalent to $922 + 1 + 1\frac{1}{2}$ or 924·5; but since 5 of silver have also been added beyond that which the alloy originally contained, the amount to be reported becomes $924{\cdot}5 - 5$, or the fineness of the bar is 919·5. It is preferable, in cases where the bars are below the standard, to add an excess of silver at once, and then to estimate the excess of silver in the manner above described; because, if, instead of acting thus, successive doses of 0·01 of silver be added until no further precipitate is formed, it becomes very difficult to render the solution clear by agitation.

The standard solution of salt is prepared at a temperature, say, of 60°, consequently the pipette, *g*, will only deliver a volume of liquid rigorously equal to 9·22 grains of silver, at that temperature. At a higher temperature the liquid will expand, and a given volume will therefore contain a smaller amount of chloride of sodium, whilst at a lower temperature it will contract, and will contain a larger amount. A correction for this variation in the strength of the liquid is therefore required. This is made very simply in the following manner. Each time that a number of assays is made, a piece of fine silver, equal to 9·25 grains, is weighed off, dissolved in nitric acid, and assayed as above directed. The number of pipettes of the decimal solution of salt which is required to complete the precipitation is noted, and the value of the contents of the large pipette, *g*, is thus verified upon each occasion. If, for example, 2½ pipettes were required for completing this precipitation, the large pipette would deliver a quantity of the solution sufficient to precipitate 9·225 grains on that day, instead of 9·22. Any deviation from the calculated value is allowed for, and a correction is made upon the assays by means of a table constructed for the purpose.

It is easy to apply this apparatus to the assay of silver of other degrees of fineness; but it is necessary to know approximatively the value of the alloy, in order that a suitable weight of it may be dissolved in nitric acid. Suppose, for instance, a number of bars approximatively of the value of 900 (the French standard) are to be assayed; a piece of the alloy, which contains approximatively 9·25 grains of fine silver, must be taken; the quantity required is easily calculated, since the weight of the alloy needed will be inversely as its fineness; for 900 : 925 : : 10 grs. : 10·277 grs. The weight required in this case will consequently be 10·277 grains.

Mercury is the only metal the presence of which interferes with the accuracy of the assay by the humid method; but the process may be modified so as to give correct results even in this case.

(797) *Preparation of Fine Silver.*—In order that the foregoing process shall be accurately performed, it is necessary to be provided with silver of absolute purity. The following is the best method of procuring the metal in this condition. Standard silver is dissolved in nitric acid: the liquid is diluted, and decanted or filtered from undissolved particles of gold or of sulphide of silver, and the solution is precipitated by the addition of a solution of chloride of sodium in slight excess. The precipitate is washed in a large jar by subsidence, until the washings are tasteless. The chloride is then mixed with oil of vitriol, in the proportion of 3 ounces to each

pound of chloride, and several bars of zinc are placed in the mass; the zinc speedily becomes converted into chloride of zinc, which is dissolved, whilst the silver is reduced to the metallic state, and by a voltaic action the reduction gradually extends through the mass; $Zn + AgCl = Ag + ZnCl$. The mixture is not to be agitated. In the course of a day or two the decomposition is usually completed. If a portion of the reduced silver, after being thoroughly washed, is entirely soluble in nitric acid, the reduction is complete. The bars of zinc, with the crust which adheres to them, are then carefully removed, and the reduced metal is digested for two days with diluted sulphuric acid, to remove any portions of the subsalts of zinc which are occasionally formed, and is washed in a large vessel by subsidence, until the washings cease to precipitate nitrate of silver.* The reduced silver is now redissolved in nitric acid, and a second time precipitated as chloride, pure hydrochloric acid being employed for this purpose: the precipitated chloride is again washed by subsidence until the washings no longer redden litmus. The chloride of silver is next dried until it ceases to lose weight, 100 parts of the chloride are mixed with 70·4 of chalk, and 4·2 of powdered charcoal, and the mixture is heated in a deep clay crucible.† The temperature is kept at a dull red heat for half an hour, after which it is gradually raised to full redness: a considerable disengagement of gas takes place, owing to the evolution of carbonic acid and carbonic oxide, and oxychloride of calcium is formed, constituting a fusible slag, beneath which the pure silver collects; $AgCl + 2\,(CaO,CO_2) + C = CO + 2\,CO_2 + CaO,CaCl + Ag$. The silver may be poured into an ingot mould, remelted in order to free it from slag, and afterwards rolled into sheets. Silver sufficiently pure for all ordinary purposes may also be obtained in a crystalline form by boiling a slightly acid solution of nitrate or other salt of silver with sheet copper: the precipitated silver is well washed, digested in a solution of ammonia, to remove any traces of adhering oxide of copper, and again washed.

(798) Oxides of Silver.—Silver forms three oxides; a suboxide, Ag_2O; a protoxide, AgO, which is the basis of the salts of the metal; and a peroxide, AgO_2, which does not combine with acids.

Suboxide of Silver (Ag_2O).—According to Wöhler, if the citrate of silver be heated to 212° in a current of hydrogen, the salt loses

* The reduced silver may be dried, and cast into ingots if desired. The metal is refined in large quantities for commercial purposes in this manner. It is not absolutely pure, and therefore, for delicate chemical operations, it undergoes the further process of purification described in the text.

† The washed chloride may also be reduced without difficulty by fusion with about half its weight of dried carbonate of soda.

half an equivalent of oxygen, and a compound is produced which is sparingly soluble in water, forming with it a brown solution, from which, on the addition of potash, a suboxide of silver is precipitated. This compound is very unstable; hydrochloric acid converts it into subchloride, but it is decomposed by other acids, and by ammonia, into protoxide of silver and metallic silver. A mixture of metallic silver and suboxide of silver is also obtained by boiling the yellow arsenite of silver with a strong solution of caustic soda, arseniate of soda being formed in the liquid:—

$$3\,AgO,AsO_3 + 3\,NaO = Ag_2O + Ag + 3\,NaO,AsO_5.$$

Protoxide of Silver ($AgO = 116$).—This oxide may be procured by adding a solution of potash or of soda to a solution of the nitrate or any soluble salt of silver. A brown hydrated oxide falls, which readily parts with its water, and if dried at a temperature above 140°, becomes anhydrous; it gives off oxygen below a red heat, and becomes reduced to the metallic state. Light also reduces it, and hydrogen, even at 212°, has a similar effect; contact under water with metallic tin or copper also deprives it of oxygen. Oxide of silver is a powerful base; it combines easily with acids, yielding salts which in some cases are isomorphous with the corresponding salts of soda. It forms with nitric acid a salt which is not acid in its reaction upon litmus. It is slightly soluble in pure water, to which it communicates a feebly alkaline reaction. Oxide of silver combines with the fusible silicates, and is sometimes employed for producing a yellow glass. Potash and soda do not dissolve the oxide, but it is freely soluble in ammonia, and the solution, by exposure to the air, deposits a black micaceous powder, which is powerfully explosive, and which has received the name of fulminating silver.

(799) *Fulminating Silver* is also produced if a concentrated solution of ammonia be digested for some hours upon freshly precipitated oxide of silver; a black powder is formed which is allowed to dry in minute quantities on separate pieces of filtering paper. The same compound is formed on precipitating an ammoniacal solution of nitrate or chloride of silver by the addition of potash. It is necessary to be aware of these facts, as it is a most dangerous substance, and might be produced unintentionally. Friction or pressure, even when under water, occasions it to explode: and when dry, its detonation often occurs without any assignable cause. Acids immediately decompose it into an ammoniacal salt, and the corresponding salt of silver. The composition of this body, owing to its dangerous character, has not been accurately determined, but

it is generally supposed to be a nitride, similar to that which is obtainable from mercury.

Peroxide of Silver ($AgO_2=124$); *Sp. Gr.* 5·474.—This compound is procured in dark-grey acicular crystals, when a dilute solution of nitrate of silver is decomposed by means of the voltaic current. The peroxide of silver accumulates upon the positive plate, but it always retains a certain quantity of undecomposed nitrate of silver. It is a conductor of the voltaic current. Acids decompose it, forming a salt of the protoxide, whilst oxygen gas escapes. It is also decomposed by ammonia, with effervescence, owing to escape of nitrogen.

(800) SULPHIDE OF SILVER ($AgS=124$); *Sp. Gr.* 7·2.—This compound is the principal ore of silver. 100 parts of this sulphide contain 12·9 parts of sulphur and 87·1 of silver. It is found native, sometimes crystallized in cubes or octohedra; at other times massive. It has a leaden-grey metallic lustre, from which it derives its mineralogical name of *silver glance.* Sulphide of silver is isomorphous with subsulphide of copper, and sometimes displaces it in certain minerals, such, for example, as polybasite, and fahlerz, or grey copper ore (741).

Silver has a very powerful affinity for sulphur. The metal becomes tarnished, owing to the formation of a film of sulphide, if it be exposed to the action of sulphuretted hydrogen in the gaseous state, even though largely diluted with air; and a black spot is immediately produced upon its surface by contact with a solution of a sulphide of one of the metals of the alkalies or alkaline earths. Sulphide of silver may be prepared by transmitting a current of sulphuretted hydrogen through solutions of the salts of silver, in which it forms a black precipitate; or it may be obtained by heating silver with an excess of sulphur in a covered crucible. The sulphide of silver fuses, and forms a dark grey crystalline mass as it cools, and the excess of sulphur is volatilized.

Sulphide of silver is soft enough to allow of its being cut with a knife; it also possesses sufficient malleability to receive impressions from a die. It is not a conductor of the voltaic current when cold, but if heated it readily transmits the current without undergoing decomposition. It is easily fusible, and if heated in closed vessels may be melted without becoming decomposed; but if roasted in the air, the sulphur is gradually converted into sulphurous acid, and metallic silver is left: during this operation a portion of it is usually converted into sulphate of silver, which afterwards requires an elevated temperature for its decomposition.

Sulphide of silver is decomposed when boiled with concentrated sulphuric acid, sulphurous acid and sulphate of silver being formed. Strong nitric acid also dissolves it by the aid of heat.* Boiling hydrochloric acid converts it into chloride of silver, with evolution of sulphuretted hydrogen. Chloride of copper converts it into chloride of silver, with the formation of subchloride of copper and sulphide of copper: this change is much facilitated by the presence of chloride of sodium in a moist state, as by its means both the chloride of silver and the subchloride of copper are dissolved at the moment of their formation. These reactions become important in the extraction of silver from its ores (790). Sulphide of silver is also decomposed when heated with the alkalies, and a similar effect is produced by igniting it with iron, copper, lead, and many other metals.

Sulphide of silver is not soluble in solutions of the sulphides of the alkaline metals; but it may be made to unite with many other metallic sulphides when fused with them. A native compound of this description is found in *red silver ore*, which is a double sulphide of silver and antimony, $3AgS,SbS_3$. In this mineral a portion of sulphide of antimony is often displaced by sulphide of arsenic.

(801) CHLORIDES OF SILVER.—There are two chlorides of silver, the subchloride Ag_2Cl, and the protochloride, AgCl.

Subchloride of Silver (Ag_2Cl) does not appear to have been obtained in a perfectly pure form. It is usually directed to be procured by digesting leaves of pure silver in a solution of chloride of copper or of perchloride of iron; it forms black scales which are not acted upon by nitric acid, but are resolved by ammonia into chloride of silver and metallic silver.

Chloride of Silver (AgCl = 143·5); *Sp. Gr.* 5·552.—This compound is found native, either crystallized in cubes, or as a compact semi-transparent mass, known by the name of *horn silver*. 100 parts of this compound contain 75·27 of silver and 24·73 of chlorine. It is procured as a dense white flocculent precipitate on adding hydrochloric acid or the solution of any chloride to a soluble salt of silver: when moist, it quickly assumes a violet colour by exposure to the sun's light; a similar change is produced gradually by diffused daylight. The subchloride appears to be formed under these circumstances, and chlorine is set free.

* Nitrate of silver forms with the sulphide a yellow compound (2 AgS, AgO, NO_5), insoluble in cold nitric acid, but it is decomposed when washed with boiling water. It is left in the form of a yellow powder when silver containing sulphide is dissolved in warm nitric acid of sp. gr. about 1·2.

If the chloride be moistened with a solution of nitrate of silver and exposed to the sun in a thin layer, a strong odour of hypochlorous acid is immediately developed.

Chloride of silver is insoluble in pure water, and in all the diluted acids. A solution of silver containing not more than 1 part of the metal in 200,000 of water is immediately rendered opalescent by the addition of hydrochloric acid. Chloride of silver is however taken up by boiling hydrochloric acid and by strong solutions of the chlorides of metals of the alkalies and alkaline earths, with which it forms crystallizable double salts; they are decomposed if their solutions are diluted; advantage is taken of this circumstance in the extraction of silver (*note*, p. 709). Chloride of silver is decomposed by digestion with a solution of bromide or of iodide of potassium, bromide or iodide of silver being produced, while chloride of potassium is obtained in solution. Field, who made this observation, has proposed to employ it for determining the proportions of chlorine, bromine, and iodine in the analysis of a mixture in which they occur together.—*Q. J. Chem. Soc.*, x. 236.

Chloride of silver melts at a temperature of about 500°, and when strongly heated is partially volatilized; on cooling it forms a horny, semi-transparent, sectile mass. It is not decomposed when heated with carbon; but is easily reduced by hydrogen if it be heated in a current of the gas, hydrochloric acid being formed, whilst metallic silver is set free: zinc, and iron, and many of the easily oxidizable metals also reduce moist chloride of silver. On the large scale this process is turned to account in the refining of silver (797). It is not necessary that the chloride of silver be freshly precipitated, though, if it be, the operation is more rapid; if a cake of the fused chloride be laid upon zinc or on iron and covered with acidulated water, it will after some days be completely reduced to a spongy mass of metallic silver.

Weak alkaline leys do not act upon chloride of silver, but if a concentrated solution of potash be boiled upon it, chloride of potassium is formed, and a dense black oxide of silver is produced; the addition of sugar to this mixture reduces the oxide rapidly to the state of metallic silver. A solution of ammonia dissolves the chloride freely, and deposits it again, by evaporation at ordinary temperatures, in transparent colourless crystals; if the solution be boiled, fulminating silver is deposited. The solid chloride absorbs ammoniacal gas rapidly, and leaves it unaltered when heat is applied (311). When chloride of silver is ignited with the carbonates of the alkalies, chlorides of their bases are formed and

pure silver is left: this reaction furnishes a means of procuring large quantities of silver in a state of purity; $AgCl+NaO,CO_2=NaCl+CO_2+O+Ag$. Chloride of silver is soluble in solutions of the hyposulphites, forming compounds of an intensely sweet taste: by evaporating these solutions crystalline double hyposulphites may be procured (348). Cyanide of potassium likewise dissolves chloride of silver, forming chloride of potassium and a double cyanide of silver and potassium. The soluble sulphites also dissolve chloride of silver.

Bromide of Silver ($AgBr=188$) constitutes a rare mineral which has been found in Chili; but it occurs in combination with chloride of silver in variable proportions in tolerable abundance at the mine of Chañarcillo, in Atacama. The bromide may be formed artificially by adding a solution of bromide of potassium to one of nitrate of silver. 100 parts of this compound contain 42·56 of bromine and 57·44 of metal. It is of a yellowish colour, is insoluble in water, and is much less soluble in ammonia than the chloride. Acids do not dissolve it, but chlorine disengages vapours of bromine from it, and chloride of silver is produced. Bromide of silver fuses below a red heat. It is soluble in a concentrated solution of bromide of potassium, and in other bromides, with which it forms double salts, which are decomposed by dilution with water. Both the bromide and the iodide of silver are soluble in a solution of hyposulphite of soda.

(802) Iodide of Silver ($AgI=235$; *Sp. Gr.* 5·5) is found in Mexico, mixed with carbonate of lime, native silver, and sulphide of lead. It may be procured artificially by precipitating a solution of the nitrate of silver by one of iodide of potassium, when a pale yellow flocculent deposit occurs, which is but slowly acted on by light, is insoluble in acids, and almost so in ammonia. It may also be obtained by acting upon metallic silver with hydriodic acid, which dissolves the metal with evolution of hydrogen, and gradually deposits six-sided prisms of the iodide: 100 parts of iodide of silver contain 54·04 of iodine and 45·96 of silver. It fuses easily into a mass which becomes yellow and opaque on cooling. It is decomposed by zinc in the presence of moisture. Chlorine displaces the iodine from the salt. Iodide of silver is soluble in a hot solution of hydriodic acid, which on cooling deposits flaky crystals of a compound of the acid with iodide of silver (AgI,HI). The iodide is likewise soluble in concentrated solutions of iodide of potassium.

Fluoride of Silver ($AgF=127$) is freely soluble in water; it

is obtained by dissolving the oxide or the carbonate of silver in diluted hydrofluoric acid, but it is partially decomposed on evaporating its solution.

(803) SULPHATE OF SILVER ($AgO, SO_3 = 156$); *Sp. Gr.* 5·322. —When silver is boiled with sulphuric acid, a portion of the acid is decomposed and gives oxygen to the silver, which is converted into a sulphate, while sulphurous acid escapes: the sulphate is dissolved by the excess of acid, but is deposited in great part on the addition of water, of which it requires 90 times its weight for solution. It may be obtained in small rhombic prisms, which are isomorphous with those of sulphate of soda. They fuse readily; for their decomposition they require a temperature higher than is needed to decompose the sulphates of iron or copper. (See *note*, p. 709.) Small quantities of gold are separated from silver on the large scale, by boiling 1 part of the alloy, finely granulated, in cast-iron vessels with 2½ parts of oil of vitriol; the gold is left behind as a fine powder. The solution of silver is afterwards diluted till of a specific gravity of 1·200, introduced into leaden vessels, and the silver precipitated in the metallic form from the solution by bars of metallic copper. This process has been economically applied to the extraction of the gold contained in old silver coin, even where the proportion of gold did not exceed 1 part in 2000. It cannot be advantageously practised upon alloys containing more than about 200 parts of gold per 1000. If copper be present, its proportion should not exceed 4 per cent. of the mass; otherwise the sulphate of copper, owing to its sparing solubility in the acid, impedes the operation. Crystallized sulphate of silver absorbs 1 equivalent of ammonia with rapidity. A hot solution of ammonia dissolves the salt freely, and on cooling deposits crystals composed of ($2\ H_3N, AgO, SO_3$).

(804) NITRATE OF SILVER ($AgO, NO_5 = 170$); *Sp. Gr.* 4·336.— This salt is readily formed by dissolving silver in moderately strong nitric acid. If standard silver be employed in its preparation, the oxide of copper is easily separated from the solution by boiling it upon freshly precipitated oxide of silver, which may be obtained by precipitating a portion of the same solution by potash, and washing the precipitate, the presence of oxide of copper being unimportant. 100 parts of the nitrate contain 31·77 of nitric acid, and 68·23 of oxide of silver, or 63·51 of metallic silver. It crystallizes in square, colourless, anhydrous tables, which require an equal weight of cold water for solution. Boiling alcohol dissolves about a fourth of its weight of the salt, but deposits most of it on cooling. The nitrate fuses at 426° when heated, and if then cast into cylindrical moulds, it forms the sticks of *lunar*

caustic employed by surgeons as an escharotic. By a more elevated temperature it is decomposed, nitrite of silver is produced, and at a still higher temperature metallic silver is left.

Nitrate of silver, when pure, undergoes no change by the action of light; but it is readily decomposed by the combined action of light and organic matter, which it usually stains black. The stain thus produced cannot be removed by washing with soap and water; from this property it has been employed as the basis of an ink for marking linen, which may be prepared as follows:—Dissolve 2 drachms of nitrate of silver and 1 drachm of gum arabic in 7 drachms of water, and colour the liquid with Indian ink (Brande). It is requisite to prepare the cloth first, by moistening the spot to be marked with a solution of carbonate of soda, which is allowed to become dry. This preparatory solution may consist of 2 ounces of crystallized carbonate of soda, and 2 drachms of gum, dissolved in 4 ounces of water.* The black stains of nitrate of silver may be removed from the hands or from linen by the employment of a strong solution of iodide of potassium; cyanide of potassium is still more effectual. Dry nitrate of silver absorbs 3 equivalents of ammonia, and if ammoniacal gas be passed into a concentrated solution of the salt, crystals having the composition ($2\ H_3N,AgO,NO_5$) are deposited.

When metallic silver in fine powder is digested in a solution of nitrate of silver, it is dissolved, and a yellow solution is formed analogous to that obtained when lead is similarly treated (766).

(805) *Triphosphate of Silver* ($3\ AgO,PO_5=419$; *Sp. Gr.* 7·321) is of a yellow colour, which is speedily changed by the action of light. The salt is very soluble in excess both of nitric acid and of ammonia. It is easily procured by precipitating a solution of the ordinary phosphate of soda by one of nitrate of silver; it fuses if heated above redness. The *pyrophosphate* ($2\ AgO,PO_5$) is obtained in like manner by precipitating the nitrate of silver by pyrophosphate of soda; it is a white precipitate slowly darkened by light, and is easily fusible. The *metaphosphate* (AgO,PO_5) is obtained by precipitation from the nitrate of silver by the metaphosphate of soda; it forms a gelatinous mass, which softens even at a heat of 212°, and is soluble in excess of nitrate of silver. If boiling water be poured upon this precipitate, it fuses; acid is removed, and a submetaphosphate is left, consisting of $3\ AgO,2\ PO_5$ (Graham).

* A solution of coal tar in naphtha forms a cheap indelible marking ink, which resists the action of chlorine, and is used by bleachers to mark their goods.

(806) CHARACTERS OF THE SALTS OF SILVER.—The soluble salts of this metal are colourless, and nearly all are anhydrous; they do not redden litmus; they have a powerfully acrid, metallic, astringent taste, and act as irritant poisons. *Before the blowpipe* they are all readily reduced on charcoal to the metallic state, especially when mixed with carbonate of soda. They give a yellowish bead with microcosmic salt in the oxidating flame. In solution the salts of silver present the following reactions:—

The *fixed alkalies* give a brown hydrated oxide, insoluble in excess of the precipitant; *ammonia,* a brown precipitate, readily soluble in excess of ammonia; *carbonates of potash and soda,* a white carbonate of silver insoluble in excess, but soluble in carbonate of ammonia. *Sulphuretted hydrogen* and *hydrosulphate of ammonia* give a black precipitate of sulphide of silver, not soluble in ammonia or in the sulphides of the alkaline metals. But the most characteristic test is the action of *hydrochloric acid* or of a *soluble chloride,* which produces a white curdy precipitate of chloride of silver, insoluble in nitric acid, but readily soluble in ammonia; it is also soluble in hyposulphite of soda, with which it forms an intensely sweet solution; cyanide of potassium also dissolves it: chloride of silver speedily assumes a violet tinge when exposed to light; this change is impeded by the presence of free chlorine as well as by that of free nitric acid, and is prevented by the admixture of a small proportion of chloride of mercury. *Iodide* or *bromide of potassium* gives a yellowish-white precipitate of iodide or of bromide of silver, sparingly soluble in ammonia. *Hydrocyanic acid* and *cyanide of potassium* give a white curdy precipitate of cyanide of silver, which is soluble in excess of cyanide of potassium, easily soluble in ammonia, insoluble in diluted nitric acid, but soluble in boiling nitric acid if concentrated. *Phosphoric, chromic, oxalic, tartaric,* and *citric* acids all form insoluble precipitates with salts of silver. Indeed, silver furnishes a greater number of insoluble salts than any other metal; they are almost all neutral in composition, and generally of a dazzling white colour. Most of them, however, blacken when exposed to the action of light. Nearly all of them are soluble in ammonia, and many of them also in nitric acid. *Many metals* reduce solutions of the salts of silver, and throw down the silver from them in a metallic state, as is beautifully shown by the action of mercury, which produces a crystalline deposit consisting of an amalgam of silver, forming what has been termed the *arbor Dianæ**. Copper and

* On one occasion I found the long prismatic thin crystals to have the composition $AgHg_2$, containing 26·45 per cent. of metallic silver.

zinc also precipitate silver from its solutions. *Phosphorus* becomes coated with metallic silver if placed in a solution of any of its salts. A solution of *protosulphate of iron* also precipitates silver in the metallic form from its solutions, if they do not contain free nitric acid. If a solution of ammonia-nitrate of silver be added to one of protosulphate of iron, an intensely black precipitate (Ag_2O, $2\,FeO,Fe_2O_3$; H. Rose) is produced. This reaction is extremely sensitive for very small quantities of iron. It is not improbable that this compound is formed when protosulphate of iron is used for developing the latent image on the photographic plate (884).

The compounds of silver exhibit a less strongly marked tendency to form double salts than is the case with the other noble metals.

(807) *Estimation of Silver.*—Silver may be estimated either in the metallic state, as in the process of cupellation,—or in the form of chloride, 100 parts of which, after fusion, correspond to 75·27 of the metal. This precipitation is best effected by acidulating the liquid with nitric acid, and adding hydrochloric acid in slight excess. After the precipitate has been collected and dried, it should be detached from the filter, and fused in a porcelain capsule; on burning the filter, the portions of chloride retained by it are reduced partially to the metallic state by the hydrogen of the paper; the ash must therefore be moistened, first with nitric, and then with hydrochloric acid, to reconvert it into chloride: the excess of acid must afterwards be expelled by heat.

(808) *Separation of Silver from other Metals.*—This is readily effected by means of hydrochloric acid. If lead be present, the solution must be diluted largely: should mercury be in solution, it must be converted into a salt of the red oxide by boiling the liquid with nitric acid, after which the silver may be precipitated in the form of chloride.

§ III. Gold (Au=196·6). *Sp. Gr.* 19·34.

(809) This valuable metal has been prized from the earliest ages of the world. It is found in small quantities in numerous localities, and always occurs, in the native state, crystallized in cubes, octohedra, or tetrahedra,—or in plates, in ramified masses, and in nodules or *nuggets*, which sometimes weigh many pounds.*

* A specimen of native gold, nearly free from earthy impurities, from the Kingower diggings, Australia, weighing 1743 oz., was exhibited in England in the early part of 1858, and still larger masses have been found subsequently.

Native gold is always alloyed with silver; small quantities of osmium and iridium, copper, antimony, and, in some rare instances, tellurium are found accompanying it. No regular veins of gold are met with; it commonly occurs either in primitive or volcanic rocks, or in the alluvial deposits of certain rivers. Its most celebrated mines are those of California and Australia; and those of Mexico, Chili, Brazil, and Peru. A good deal of gold is also obtained from the Ural Mountains: many of the rivers of Africa likewise contain it among their sands, as do those of Hungary, Transylvania, and Piedmont. In these countries it is principally extracted from the river sands by gipsies.

Extraction.—The operations for obtaining gold from its deposits differ from those required by almost every other metal, in being for the most part purely mechanical.

Much of the gold in circulation, before the discovery of the deposits in Australia and California, was obtained from auriferous pyrites. This mineral is coarsely pulverized, either before or after roasting, and washed: the heavier particles of gold subside, and are extracted from this concentrated portion by amalgamation, the excess of mercury being separated by distillation. Various methods are adopted for washing the auriferous material: in Mexico this operation is usually performed by negresses, who having pulverized the ore under flat stones, agitate it in wide, shallow, wooden dishes, separating the lighter portions with much dexterity. In Europe, the pyrites is ground and amalgamated, in mills constructed for the purpose. Those who wash the river sands usually select some spot at a bend of the stream, where the mud appears to be black or reddish; as it is here, if anywhere, that the gold is found. The most favourable time is when the waters are subsiding after storms or heavy rains; the sand is concentrated either by washing it in shallow vessels, or else by allowing it to pass through a succession of troughs. Amalgamation is afterwards resorted to, and the product is distilled, as in the analogous process for obtaining silver.

(810) *Properties.*—Gold is of a rich yellow colour and high metallic lustre. It is not remarkable for its hardness, being, when in a pure state, nearly as soft as lead. Its tenacity, however, is considerable, ranking next to silver, so that it may be drawn into very fine wire. As already mentioned, it is the most malleable of the metals, and so extreme is the thinness to which it may be reduced by hammering, that 280,000 leaves placed one upon another would be required to occupy the thickness of one inch. The thickness of the film may be still further reduced by floating it

upon a dilute solution of cyanide of potassium. Faraday found that such a film when attached to a plate of glass still retained its power of reflecting yellow light and transmitting green: if, however, the temperature were maintained for a short time at a point not exceeding 600° F., the metallic lustre disappeared entirely, and the transmitted light became of a pure ruby red. The pressure of agate, or of any hard body upon the film, changed the colour of the transmitted light at that spot again to green. (*Phil. Trans.* 1857.) Gold fuses at a temperature of 2016°. It cannot be advantageously employed for castings, as it shrinks greatly at the moment of solidifying. It is but very slightly volatile in the heat of the furnace, though by a powerful electric discharge, by the concentration of the sun's rays with a large convex lens, or by the intense heat of the oxyhydrogen jet, it may be dispersed in purple vapours. It is one of the most perfect conductors both of heat and of electricity. Gold suffers no change by exposure to air and moisture at any temperature. None of the simple acids, with the exception of the selenic, have any effect upon it, but it is dissolved by any mixture which liberates chlorine. Its usual solvent is aqua regia, which for this purpose is generally prepared by mixing 1 part of nitric acid and 4 parts of hydrochloric acid. The alkalies do not affect it; a crucible of gold is consequently a valuable instrument in the analysis of minerals which require fusion with the caustic alkalies. The metal combines directly with fluorine, chlorine and bromine, without the aid of heat, and with phosphorus when heated.

(811) *Preparation of Fine Gold.*—Gold is best obtained in a state of purity by dissolving the metal in aqua regia, and evaporating the solution of chloride of gold thus obtained with an excess of hydrochloric acid, for the purpose of destroying the excess of nitric acid: the solution is then largely diluted with water, and decanted from chloride of silver, which is thus precipitated. A solution of protosulphate of iron is next prepared and added to the solution of chloride of gold: 1 part of gold requires between 4 and 5 parts of the crystallized protosulphate. Metallic gold is thus precipitated in the form of a finely divided powder, which, when suspended in water, is brown by reflected, but purple when viewed by transmitted light. The reaction which occurs between the chloride of gold and the protosulphate of iron is represented in the annexed equation:—

$$6\,(FeO,SO_3) + AuCl_3 = 2\,(Fe_2O_3,3\,SO_3) + Fe_2Cl_3 + Au.$$

For commercial purposes it would be sufficient now to collect

the gold, dry it, and after fusing it with borax, to cast it into ingots; but when required to be perfectly free from silver, the gold is not melted at this stage, but the precipitated metal is boiled with hydrochloric acid of sp. gr. 1·1. The acid is decanted, and the residue is boiled twice with fresh acid without washing the gold between these successive additions of acid. The last traces of iron and nearly all the chloride of silver are thus removed. The gold is then washed, dried, and mixed with its own weight of bisulphate of potash, and fused in a Hessian crucible. The last portions of chloride of silver are thus removed, and the gold is perfectly pure. When thus prepared its surface often exhibits a crystalline appearance, being embossed with aggregations of tetrahedra if the metal be allowed to cool slowly.

Levol prefers to precipitate the gold from an acid solution of its chloride by means of an acid solution of terchloride of antimony: $3\ SbCl_3 + 2\ AuCl_3 = 3\ SbCl_5 + 2\ Au$. The hydrochloric solution retains any traces of chloride of silver which may be present.

Uses.—Gold is employed in its finely divided state for gilding porcelain, which is first painted with an adhesive varnish and allowed to become partially dry; the powdered metal is then dabbed on with a dry pencil (having been previously mixed with a fusible enamel), after which the article is fired; the gilt portions are subsequently burnished, and take a high polish. It communicates a fine ruby colour to glass, and is the colouring ingredient in the beautiful red glass manufactured in Bohemia. The uses of gold in the fabrication of ornamental articles and in coinage are well known; like silver, it is too soft to be employed in a pure state.

(812) *Gilding* upon woodwork, papier mâché, or plaster is effected by means of gold-leaf, which is attached to the surface by an adhesive varnish, such as gold-size. Gilding upon metals is effected either through the medium of mercury, as in one of the processes for silvering (792), or by voltaic action, as in the process of electro-silvering already mentioned; for this purpose, a solution either of the cyanide of gold and potassium, or of oxide of gold in sulphite of potash, is used (878).

Some years ago, a means of gilding by immersion was introduced by Mr. Elkington, by which copper trinkets and stamped articles can be coated with a thin film of gold; this method has been very largely practised. The process has been carefully investigated by Barral (*Ann. de Chimie*, III., xviii. 5). The gilding bath is prepared by dissolving 1 part of fine gold in aqua

regia, and expelling the excess of acid by evaporation; the chloride is dissolved in a small quantity of water; to this solution 30 parts of bicarbonate of potash are gradually added. This liquid is then mixed with a solution of 30 parts more of the bicarbonate, dissolved in 200 parts of water, and the liquid is boiled for two hours: during this operation, the bicarbonate of potash is converted into the sesquicarbonate, and the yellow liquid passes into green; after this, the solution is ready for use. The trinkets having been annealed are cleansed from adhering oxide by a momentary immersion in a mixture of equal parts of sulphuric and nitric acids, to which, when the gold is intended to have a *dead* appearance, a little common salt is added. The articles are washed in water and then plunged into the hot gilding liquid, where they are left for about half a minute, after which they are washed in water and dried in hot sawdust. The layer of gold deposited in this operation is always excessively thin, and cannot be increased, because as soon as the alloy is once covered with a film of gold no further deposition occurs. This bath may be also employed for gilding on German silver, platinum, or silver, by immersing the objects composed of these metals in the liquid in contact with wires of copper or of zinc. During this process of gilding, a remarkable reaction occurs,—the gold imparts a portion of its chlorine to the excess of potash contained in the bath, forming chlorate of potash; protochloride of gold is formed and is decomposed by the copper, chloride of copper being produced, whilst metallic gold is deposited upon the surface of the trinkets: $6\ AuCl_3 + 6\ KO + 12\ Cu = 12\ CuCl + 5\ KCl + KO,ClO_5 + 6\ Au$. In the course of the operation a black powder is precipitated, which contains hydrated carbonate of copper, mixed with a small proportion of the purple of Cassius derived from the action of the gilding solution upon the tin contained in the solder of the trinkets.

With mercury, gold forms a semi-solid amalgam of a yellowish colour, which is soluble in an excess of mercury. This excess may be removed, as in the case of silver amalgam, by filtering and squeezing it through chamois leather. It is this amalgam which is formed during the extraction of gold from its ores; it is also extensively prepared for the purposes of gilding. A combination of mercury with gold (Au_4Hg) may be obtained crystallized in brilliant four-sided prisms by acting with diluted nitric acid, aided by a gentle heat, upon an amalgam of gold containing about 1 part of gold to 1000 of mercury (T. H. Henry): these crystals are insoluble in nitric acid.

(813) *Alloys of Gold.*—The ductility of gold is much impaired

by alloying it with other metals, though its hardness and sonorousness are increased: these alloys are generally formed without difficulty. If a proportion of tin, of cobalt, of nickel, or of zinc, greater than 2 per cent. of the mass be present in the alloy, it is unfit for coinage; and still smaller quantities of lead, of antimony, or of bismuth render gold brittle. Palladium is a still more inconvenient impurity, since it not only renders the gold brittle, but it requires special treatment in order to extract it, as it is not removed by the ordinary operations of the refiner. A similar remark is applicable to the alloy of platinum with gold. Small quantities both of platinum and of palladium render the gold nearly white. The native alloy of osmium and iridium which frequently accompanies the Californian gold, does not combine with the metal, but remains disseminated through it in distinct grains after the gold has been melted. These grains occasion much inconvenience; they often escape notice until the metal passes through the coining press, where they make themselves apparent by their hardness, and by the injury which they consequently inflict upon the dies.

Silver and gold may be alloyed with each other in all proportions. This alloy has a pale greenish-yellow colour, which becomes nearly white when the quantity of silver exceeds 50 per cent. The malleability of gold is less diminished by the presence of silver than by that of any other metal. In the arts it frequently becomes necessary to separate these two metals, and this is usaally effected by the method termed *quartation*, or *parting*. This operation depends on thė solubility of silver in nitric acid, and the insolubility of gold in this liquid. It is necessary that the silver should amount to at least three times the weight of gold, otherwise portions of silver would be mechanically protected from the action of the acid, and the separation would be incomplete. If, therefore, the alloy be found to contain more than a fourth of its weight of gold, sufficient silver is added to reduce it to this proportion, and hence the origin of the term 'quartation.' The metals are fused together, granulated by being poured into water, and they are then digested in the acid. The gold is afterwards melted into ingots, the silver is precipitated as chloride, by common salt, and the chloride is reduced either by zinc (797), or by fusion with an alkali (801). On the large scale sulphuric acid is usually substituted for nitric acid; it is much cheaper, and is quite as effectual in dissolving the silver if boiled upon it (803).

The most useful alloy of gold is that which it forms with copper: it is of a redder colour than pure gold, and considerably harder and more fusible, but it is less ductile and malleable. It is

this alloy which is used for coinage. British standard gold contains 8·33 per cent. of copper, or 11 parts of gold to 1 part of copper. The specific gravity of this mixture is 17·157, the two metals expanding a little when they unite. In France and in the United States the standard gold contains 10 per cent. of copper. Jewellers frequently alloy their gold with a mixture of copper and silver. The alloys of gold and copper, when once the materials have been well mixed, do not exhibit the tendency to liquation which occasions so much trouble in the case of silver (794). The solder used for uniting pieces of gold is an alloy of gold with copper, which melts at a lower temperature than pure gold.

(814) *Assay of Gold.*—In the assay of gold, a combination of the processes of cupellation and quartation is employed. In the cupellation of gold the quantity of lead which is needed is about double that employed for silver; 1 part of copper requiring about 32 parts of lead. The assay of gold furnishes results which are more accurate than those obtained in the cupellation of silver. The loss of gold by volatilization is very much smaller, and scarcely any of the metal is carried into the cupel by an excess of lead.

The following is an outline of the method adopted in the assay of gold:—The quantity of the alloy for assay having been accurately weighed, it is wrapped in a piece of paper, with a proportion of silver equal to about 3 times that of the gold which the alloy is supposed to contain,* and this is submitted to cupellation in the manner already described when speaking of the assay of silver (795). By this means the silver and the gold become thoroughly incorporated, and the copper is oxidized and absorbed by the cupel with the oxide of lead. The auriferous button is then hammered into a flattened disk, about the size of a sixpence, and annealed, by heating it to redness. It is next passed between a pair of

* An approximative estimate of the composition of the alloy is sometimes made by the use of the touchstone, though it is seldom employed by the practised assayer:—A number of pieces of alloy are formed containing known quantities of gold and copper, or of gold and silver: the first consisting of pure gold; the second of 23 of gold and 1 of copper; the third of 22 of gold and 2 of copper, and so on; the assayer selects one of these alloys, or 'needles,' which from its colour he judges to approach nearest in composition to the alloy which he is about to assay; this he rubs upon a hard, black stone, the 'touchstone,' which is a peculiar kind of bituminous quartz formerly obtained from Lydia, in Asia Minor; black basalt, however, may be employed for the purpose: the alloy leaves a streak upon the stone, the colour of which is redder in proportion as the copper preponderates. The streak formed by the alloy for assay is then compared with that of the needles, until one of these is found to which it nearly corresponds. The judgment may be further aided by moistening the streaks obtained, with a little nitric acid, which attacks the copper or silver, but leaves the gold.

laminating rollers, by which its thicknesss is reduced to that of an ordinary address card, after which it is a second time annealed. These operations render it sufficiently flexible to allow of its being coiled into a small spiral by rolling between the finger and thumb. The *cornet* thus obtained is next introduced into a flask which contains about an ouncc of nitric acid of sp. gr. 1·180, heated nearly to the boiling point. Brisk evolution of nitrous fumes immediately ensues; the silver is gradually dissolved away, and the gold is left in the form of the original cornet, as a brown, porous, very brittle mass. After this first boiling has been continued for 10 minutes, the flask is removed from the fire, the acid solution is poured off, and the cornet is washed by carefully pouring distilled water upon it; which, after standing for a couple of minutes, is again poured off. Some traces of silver are, however, still retained by the gold, and, in order to remove these, the cornet is again boiled with nitric acid, which, this time, must be of sp. gr. 1·280. In this second boiling, which must be continued for 20 minutes, a small fragment of charcoal should be introduced into the flask, in order to prevent the ebullition from taking place irregularly, with sudden bursts, as it is very apt to do if this precaution be neglected.

The acid having been poured off, the flask is filled up completely with distilled water. A small, smoothly finished, porous clay crucible is placed over the mouth of the flask, and the flask and crucible are inverted, so that the cornet shall fall gently through the water into the crucible: by a dexterous movement of the hand, the flask is then withdrawn in such a manner as to prevent the overflow of any liquid from the little crucible: the water is afterwards carefully poured off from the cornet, and the crucible is heated to redness in the muffle. By this means the gold, though it is not fused, is rendered much more compact; it shrinks in bulk, loses its brown appearance, and assumes the peculiar colour and lustre of the metal. When cold, the cornet is weighed with the same precision as the original alloy. The assayer calls the arbitrary weight of the alloy upon which he operates, 1000; his weights are all subdivided so as to give him the value of the alloy in thousandths of this original quantity; so that if he find a portion of the alloy which originally weighed 1000 of these arbitrary units, to yield a quantity of gold equal to $916\frac{2}{3}$ of these parts, he reports it as 916·6. 1000 ounces of such an alloy would contain 916·6 ounces of fine gold.

The amount of alloy upon which it is most convenient to operate in assaying is half a gramme, or between 7 and 8 grains.

The gold contained in the cornet is never absolutely pure: it retains a small quantity of lead and of silver, and frequently also traces of copper, which render its weight a little higher than it ought to be. In order to ascertain the amount of this error, a number of *proofs* are passed through the muffle simultaneously with the alloys, and subjected to the same process as the alloys themselves. These proofs consist of weighed portions of fine gold, to which are added a proportion of copper equal to that estimated to exist in the alloys under examination. The excess of weight which these proofs indicate shows the amount of the correction which it becomes necessary to make. This correction is liable to daily variation, according to the temperature of the furnace, the more or less perfect softening of the buttons during annealing, the thickness of the cornets, &c.; but it usually varies from 0·2 to 0·5 parts in 1000. Most assayers vary the quantity of lead according to the proportion of copper in the alloys. I have found it advantageous to use the same amount of lead in all cases; the correction then becomes uniform for all the assays passed at one operation.

When the alloy contains very little copper, as commonly occurs with native gold, the button of alloy is liable 'to spit' as it cools after the cupellation; this mischance may easily be prevented by the addition of a small fragment of copper, not exceeding $\frac{3}{4}$ of a grain in weight, before introducing the alloy into the cupel.

It frequently happens that it is necessary to ascertain the proportion both of gold and of silver in a given alloy. If the proportion of gold preponderate, the quantity of gold is determined in the manner above described, and that of the gold and silver together is ascertained by submitting a portion of the alloy to cupellation with lead, as if it consisted of silver only (795). The two metals, gold and silver, remain upon the cupel, whilst the copper and more oxidizable metals are absorbed. The weight of the residual button gives the united weight of the gold and silver, and the difference between this weight and that of the gold alone will of course furnish the proportion of silver.

When the proportion of gold is very small compared with that of the silver, the two metals are treated with nitric acid at once (without submitting them to the usual assay for gold); the acid dissolves the silver and other metals which may be present, leaving the gold in the form of a black powder: this powder must be collected by subsidence in one of the small porous crucibles used for annealing gold cornets, in which it is ignited, and can afterwards be weighed without difficulty.

(815) OXIDES OF GOLD.—There are two oxides of gold: a protoxide AuO, and a teroxide AuO_3: the latter possesses acid properties, and is frequently termed auric acid.

The *protoxide* ($AuO = 204{\cdot}6$) is obtained as a dark green powder by precipitating the protochloride of gold by a dilute solution of potash; it is slightly soluble in excess of the alkali: when digested with ammonia it forms fulminating gold: hydrochloric acid converts it into metallic gold and terchloride of the metal. Protoxide of gold undergoes a suspension in pure water, and passes through the filter; but boiling the solution after adding any saline compound causes its precipitation.

Teroxide of Gold; Auric Acid ($AuO_3 = 220{\cdot}6$).—This compound is best obtained by decomposing a solution of the terchloride of gold by magnesia; for if the alkalies be used, they adhere strongly to the precipitate: it falls in combination with the earth, which may be removed by means of diluted nitric acid, and the oxide of gold remains as a yellow hydrate, if the acid used be weak, or as a brown anhydrous oxide if strong; it is very readily reduced by exposure to light, and at a temperature of about 470° it is resolved into metallic gold and free oxygen. It is taken up by strong nitric and sulphuric acids, but no true salts are formed; the oxide being deposited again from these solutions in a pure state on dilution. Teroxide of gold is dissolved by hydrochloric, hydrobromic, and hydriodic acids, forming terchloride, terbromide, and teriodide of gold.

When hydrated it combines readily with the alkalies, forming salts that have been termed *aurates*, which are soluble in water, and form yellow solutions. *Aurate of potash* crystallizes in yellowish needles ($KO,AuO_3 + 6\,Aq$): its solution may be used in electro-gilding. Most of the compounds of auric acid with the earths and other metallic oxides are insoluble.

Auric acid forms with ammonia a dark olive-brown fulminating compound, analogous to that furnished by silver (799); the same compound may be formed by adding ammonia to the terchloride, but in this case it is of a reddish-yellow colour, owing to the admixture of a little ammoniacal subchloride of gold. So great is the affinity of auric acid for ammonia that it decomposes the neutral salts of the alkali, such as the sulphate, and sets their acid at liberty.

(816) *Bisulphide of Gold*, ($AuS_2 = 228{\cdot}6$).—When a current of sulphuretted hydrogen is transmitted through a cold solution of terchloride of gold, a black precipitate is produced, which, according to Levol, is a bisulphide, or rather AuS,AuS_3. It is soluble

in the solutions of the sulphides of the alkaline metals: its solution in sulphide of sodium yields a colourless salt which is soluble in alcohol; it crystallizes in six-sided prisms, consisting of (NaS, AuS + 8 Aq; Yorke), the bisulphide of gold having been converted into the protosulphide, whilst the second equivalent of sulphur has entered into combination with the excess of the alkaline sulphide. If finely-divided gold be heated with sulphur in contact with carbonate of potash, a double sulphide of gold and potassium is formed; it resists a red heat, and is very soluble in water: this sulphur salt is used for gilding china, and produces the colour known as *Burgos lustre.*

(817) CHLORIDES OF GOLD.—Gold forms two compounds with chlorine,—a protochloride AuCl, and a terchloride $AuCl_3$.

Protochloride of Gold (AuCl=232·1).—When terchloride of gold is exposed to a gentle heat, it fuses, without undergoing decomposition; but if the temperature be raised to about 350°, chlorine is gradually expelled, and a pale yellow, sparingly soluble powder is left, which is the protochloride. It is an unstable compound, but it may be washed with cold water to remove any undecomposed terchloride; boiling water converts it into a mixture of the terchloride with metallic gold, and a similar change is produced by exposing it to light. If the temperature be raised a little beyond 400°, the whole of the chlorine is expelled.

Terchloride of Gold ($AuCl_3$=303).—This compound is produced when the metal is dissolved in aqua regia; on evaporating the solution to dryness at a temperature not exceeding 300°, this salt remains behind as a red deliquescent mass. It forms with water an orange-coloured solution, which preserves its colour even when very largely diluted; alcohol also dissolves the chloride, and ether takes it up so freely as to separate it from its aqueous solution when agitated with it. Chloride of gold forms a crystalline compound with hydrochloric acid; it also unites with the chlorides of many of the basylous metals to form double salts: that with potassium crystallizes in efflorescent striated prisms, consisting of KCl, $AuCl_3$ + 5 Aq; that with sodium forms four-sided prisms, with 4 Aq. The chlorides of most of the organic bases also form crystallizable double salts with terchloride of gold: these compounds are often employed to determine the combining number of the organic alkali. The chloride of gold is easily reduced by many substances; the reaction of protosulphate of iron has already been mentioned (811). Oxalic acid produces a similar precipitate of metallic gold; thus, $2\,AuCl_3 + 3\,(2\,HO,C_4O_6) = Au_2 + 6\,HCl + 12\,CO_2$: the powder, when viewed by reflected light, appears to be

of a brown colour, but by transmitted light, whilst suspended in water, it has a purple tint. Many organic substances, if moistened with a solution of the chloride of gold, also exert a reducing effect upon it; hence the fingers or writing paper, if washed over with the solution, become stained of a violet colour when exposed to the sun's light. Metallic gold is also readily obtained from the solution of this salt by other means. A current of sulphurous acid precipitates the gold completely. Phosphorous and hypophosphorous acids, and solutions of their salts, produce the same effect; and a similar result is obtained by contact with many of the metals, such as copper, iron, and zinc. A stick of phosphorus when immersed in a solution of chloride of gold soon becomes coated with the reduced metal; and if a few drops of a solution of phosphorus in ether, or in bisulphide of carbon, be mixed with a very dilute solution of neutral chloride of gold, containing from 0·6 to 1·0 of a grain of the metal in a quart of water, the gold will be reduced in the course of a few hours. Provided that the bottle containing the solutions be chemically clean, the metal will be separated in particles of such extreme tenuity that it will remain suspended in the liquid for months; giving to it a ruby red or amethystine colour when viewed by transmitted light, though it appears to be turbid and brown when seen by reflected light. If the red liquid be mixed with a small quantity of a solution of common salt, the ruby tint is immediately changed to purple, the state of aggregation of the metal undergoing an instantaneous alteration, in consequence of which the liquid becomes colourless in a few hours, and the whole of the suspended particles of gold are deposited in a purple but perfectly metallic powder (Faraday).

A *terbromide* of gold may be formed; it crystallizes easily, and forms numerous double salts with other soluble bromides.

There are two *iodides* of gold, corresponding to the chlorides. The protiodide is a yellow insoluble powder. The teriodide is unstable; it is green and sparingly soluble; it forms double salts with the iodides of the alkaline metals.

(818) *Purple of Cassius.*—When a mixture of protochloride and perchloride of tin very much diluted is added drop by drop to a dilute neutral solution of terchloride of gold, a flocculent purple deposit takes place. The same compound is readily formed by digesting metallic tin in a neutral solution of terchloride of gold; metallic gold and the purple of Cassius being formed. The true nature of this compound has been the subject of much discussion. Berzelius concluded from the researches of Figuier (*Ann. de Chimie,* III. xi. 354) that it consists of a hydrated double stannate of gold

and tin ($AuO,SnO_2+SnO,SnO_2+4\,Aq$). Purple of Cassius undergoes a suspension in pure water, and passes through the filter, but it is separated on adding a salt to the liquid and boiling it. It is insoluble in solutions of potash and soda, but soluble in ammonia, forming a deep purple solution, from which it is deposited unchanged if the ammonia be expelled by heat, or neutralized by an acid. This solution is bleached by the action of light, and gold is deposited. Purple of Cassius is decomposed by the acids, metallic gold being left; but it is not changed by the action of light. If heated to redness, water is expelled, and a red powder is left, which is a mixture of metallic gold and peroxide of tin. Purple of Cassius, when mixed with a little borax or some fusible glass, and applied to the surface of china, imparts to it a beautiful rose or a rich purple colour. It is this compound which is added as the colouring material in the red glass of Bohemia.

(819) CHARACTERS OF THE SALTS OF GOLD.—The salts of gold are recognised by the brown precipitate of metallic gold produced by *protosulphate of iron* in their neutral solutions; and by the formation of the purple of Cassius on adding to them a mixture of *protochloride* and *perchloride of tin*. *Metallic tin* yields the same precipitate, and is a still more delicate test. Salts of gold are reduced to the metallic state by boiling their acidulated solutions with a soluble *oxalate* or *sulphite*. *Subnitrate of mercury* also gives a dark brown precipitate of reduced gold. All the salts of gold are decomposed when ignited in the open air.

(820) *Estimation of Gold.*—Gold is always estimated in the metallic state. It may readily be separated from all the preceding metals by precipitating its solution by means of a solution of protosulphate of iron, after acidulating it with hydrochloric acid. The precipitate is collected upon a filter, ignited, and weighed as pure gold.

§ IV. PLATINUM ($Pt=98{\cdot}56$). *Sp. Gr.* 21·5.

(821) PLATINUM, *little silver*, as its name implies, is a metal which is found in but comparatively few places: it was not recognised as a separate metal until Wood, an assayer of Jamaica, in 1741, pointed out its distinctive characters. It always occurs in the native state, usually in small flattened grains, in which it is mixed with palladium, rhodium, osmium, ruthenium, and iridium, —metals which are rarely found except when associated with platinum. Occasionally it occurs in larger nodules, frequently

alloyed with gold, and traces of silver, and with copper, iron, and lead. The deposits of platinum are for the most part met with in alluvial districts associated with the débris of the earliest volcanic rocks. Platinum is chiefly supplied from the mines of Mexico, Brazil, and of the Ural Mountains. It has also been met with in California and Australia. It is separated by washing from the lighter impurities contained in its ore.

Extraction.—On account of the extreme infusibility of platinum, it requires a mode of manipulation which is complicated and peculiar. 1.—The method ordinarily employed was contrived by Wollaston:—The ore, which usually contains from 75 to 85 per cent. of platinum, is treated first with nitric acid, and then with hydrochloric acid in order to remove the more easily oxidizable metals, after which it is digested in diluted aqua regia as long as anything is dissolved, the solution of the platinum taking place very slowly. The clear liquid is then decanted, and a solution of sal ammoniac is poured into it; the greater part of the platinum is thus precipitated in the form of a yellow double salt ($H_4NCl,PtCl_2$), which is sparingly soluble. The mother-liquor still retains a portion of platinum, which is precipitated by means of metallic iron; the black powder is redissolved in aqua regia, and precipitated by the addition of sal ammoniac, the double salt thus obtained being added to the first crop. The chloride of platinum and ammonium is then washed, and heated to redness, by which means the ammonia and chlorine are expelled, leaving the platinum behind in porous slightly coherent masses: this *spongy platinum* is powdered in a wooden mortar and rubbed into a magma with water, in which state it is thoroughly washed; the metallic particles soon subside, and the lighter impurities are carried away.* This metallic mud is next poured into a somewhat conical brass mould, closed below with blotting-paper loosely supported by a plug; the greater part of the water drains off, and the whole is then subjected to the action of a very powerful press. The mass which previously was of a dull grey colour, now assumes a compact metallic appearance, and acquires a specific gravity of about 10; it is next exposed to an intense heat in a wind furnace, and the ingot is forged by hammering it upon its two ends,—never upon its sides, as if this were done it would split. This heating and forging is several times repeated until it becomes

* Platinum thus prepared usually retains a small quantity of iridium, which accompanies the double chloride of platinum and ammonium. The platinum may be freed from this impurity by the method described in paragraph (846).

homogeneous and ductile; it then has a specific gravity of about 21·5. Wollaston's process for working it depends upon its property of welding at very high temperatures. Deville and Debray, in their important memoir on platinum and the metals which accompany it (*Ann. de Chimie*, III. lvi. 385), recommend fusion of platinum by means of the oxyhydrogen blowpipe, in a cavity formed in a mass of lime, for the purpose of freeing commercial platinum from the silicon and osmium which it always contains.*

2.—Deville and Debray have introduced an entirely new method for the extraction of platinum from its ores, of which the following is an outline:—A small reverberatory furnace, the bed of which is composed of a hemispherical cavity of fire-brick, lined with clay, is heated to full redness, and a charge consisting of 2 cwt. of the platinum ore, mixed with an equal weight of galena, is added in small quantities, stirring with iron rods until the platinum and lead have combined into a matt. A small quantity of glass is thrown in to act as a flux, and by degrees a quantity of litharge equal in weight to the galena employed is added. The sulphur is thus completely oxidized and expelled, and the lead of the

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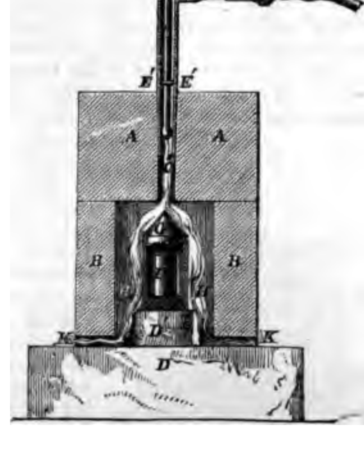
* Deville and Debray employ the oxyhydrogen blowpipe in the following manner, for effecting the fusion of platinum and of the refractory metals which accompany it. The apparatus consists of the blowpipe, C, a furnace, A B D, and a crucible, G H I. The blowpipe is composed of a copper tube half an inch in diameter, terminating below in a slightly conical platinum jet about an inch and a half long. Within this tube, which is supplied with hydrogen through the stopcock, H, is a second copper tube, c′, terminated also by a platinum nozzle with an aperture of about a twelfth of an inch in diameter.

FIG. 346.



The furnace, A B D, consists of three pieces of well-burnt lime of slightly hydraulic quality, which can be turned at the lathe with ease. The cylinder, A, is about 2½ inches thick, and is perforated with a slightly conical tube, which accurately fits the blowpipe and allows it to pass about half way through the thickness of the mass. A second somewhat deeper cylinder of lime, B, is hollowed into a chamber sufficiently wide to admit the crucible and leave an interval of not more than a sixth of an inch clear around it. At K K are four apertures for the escape of the products of combustion.

The outer crucible, H H, is also made of lime, but it contains a smaller crucible, I, of gas coke, provided with a cover of the same material; and in

galena and the litharge reduced to the metallic state, when it forms an easily fusible alloy with the platinum. The melted mass is now left completely at rest for some time. The osmide of iridium (which is not attacked at all during the operation) gradually sinks to the bottom of the liquid alloy, and the upper portions of the platiniferous lead are cautiously decanted from it by iron ladles, and cast into ingot moulds. The residue, containing the osmide of iridium, is added to a subsequent melting.

The platiniferous lead is then submitted to cupellation in the ordinary manner, and the crude metallic platinum left after cupellation is refined by fusion on a bed of lime, by means of the oxyhydrogen blowpipe: after undergoing this operation it furnishes platinum, nearly pure, and very ductile and malleable.

The alloy of platinum, iridium, and rhodium is well adapted to the preparation of crucibles, as if the proportions of the metals be properly adjusted, this alloy is harder and resists a higher temperature than pure platinum; at the same time it is less easily attacked by chemical agents. Such an alloy may be obtained from the crude platinum ore by simply fusing it by the oxyhydrogen blowpipe upon a bed of lime with a quantity of lime equal in weight to the amount of iron in the ore. Palladium and osmium are volatilized during this process of fusion, whilst the copper and iron become oxidized, and form fusible compounds with the lime.

(822) *Properties.*—Platinum is a white metal susceptible of high lustre, and when pure is about as hard as copper. In ductility it rivals iron, and in tenacity it is inferior only to iron, cobalt and nickel, and perhaps copper. It resists the highest heat of the

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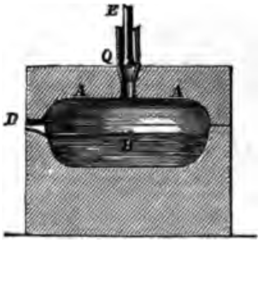
this the substance to be fused is placed, the crucible resting on the lime-support D′. The conical cover, G, is made of lime, and its apex should be placed exactly under the blowpipe jet, at a distance from it of from ¾ to 1¼ inch.

The different pieces of the furnace must be bound round with thin iron wire to support them when they crack. The oxygen is admitted under a pressure of a column of 16 inches of water. The temperature is gradually raised to the maximum, and in about 8 minutes from this time the experiment is complete.

Fig. 347.



By employing a jet of mixed coal gas and oxygen (E Q Fig. 347) in a furnace of lime, A B, provided with lip at D for pouring, Deville and Debray succeeded, at an expense of about 43 cubic feet of oxygen, in melting and refining in 42 minutes, 25·4 lb. avoirdupois of platinum, and casting it into an ingot in a mould of gas coke. Lime is so bad a conductor of heat that, if a cup of lime not more than 0·8 inch thick be filled with melted platinum, the exterior scarcely rises beyond 300° F.

forge; but it may be fused by the voltaic battery or by the oxyhydrogen blowpipe, before which it is volatilized, and is dispersed with scintillations. Deville and Debray state that it absorbs oxygen, and if melted in considerable masses spits like silver on rapid cooling. Attempts to crystallize platinum artificially have not succeeded, but very perfect octohedra have been met with in its native beds. Its specific gravity differs somewhat with the mode of manipulation to which it has been subjected, but it varies between 21 and 22, being (with the exception of iridium and osmium, which are equally dense) the heaviest form of matter as yet known. It expands less by heat than any other metal, and in its power of conducting heat and electricity it is much inferior to gold and silver,—in these respects ranking very near to iron.

Platinum does not undergo oxidation in air at any temperature: none of the acids have singly any effect upon it; aqua regia dissolves it, though but slowly. If heated to redness in air in contact with the alkalies or alkaline earths, especially with lithia or baryta, it is corroded, owing to the formation of an oxide which combines with the alkaline base. When phosphorus is heated with spongy platinum, combination between them takes place readily. The affinity of sulphur for platinum is much less powerful. Dry chlorine is without action upon this metal, even when aided by heat.

(823) *Platinum Black.*—Platinum may be obtained in a state of subdivision still finer than that in which it is left on heating the double chloride of platinum and ammonium. In this form it has the appearance of soot, and is termed *platinum black.* It may be procured in this condition by several methods, of which one of the most efficacious consists in dissolving the protochloride of platinum in a strong solution of caustic potash, and adding alcohol to the hot liquid which is placed in a capacious vessel, and kept constantly stirred: brisk effervescence takes place, owing to the escape of carbonic acid; the platinum is reduced, and is deposited as a black powder, which requires repeated washing,—first with alcohol, next with potash, then with hydrochloric acid, and lastly with water. Platinum, in this finely divided state, greedily condenses oxygen from the air, and absorbs many times its bulk of the gas. If moistened with alcohol or ether it imparts this oxygen to them, and forms new compounds; whilst the powder glows from the heat which is extricated. In all its states, platinum possesses, in a marked degree, this property of condensing gases upon its surface; and the more finely it is divided, and consequently the larger the surface which it presents, the more striking is the phenomenon.

(824) *Uses.*—The most important applications of platinum are confined to the laboratory of the manufacturing and experimental chemist; they depend upon its great infusibility, and its power of resisting chemical agents. Its introduction as a material for the construction of apparatus employed by the analytical chemist has contributed in no small degree to the rapid progress of the science during the last forty or fifty years, by conferring upon its experiments a precision, neatness, and accuracy till then unattainable. In the concentration of oil of vitriol, large platinum stills are frequently employed; some of these vessels weigh upwards of 1000 ounces. It is found expedient to gild these vessels upon their inner surface, for, unless this precaution be adopted, the stills when made of platinum prepared by Wollaston's method, after a short time become sufficiently porous to allow the acid to transude. An attempt was made in Russia to employ platinum for coinage, but it was found to be inconvenient, and the experiment has been abandoned. Platinum is sometimes used for the touch-holes of fowling pieces.

Alloys.—Platinum may be easily alloyed with many of the more fusible metals, the combination generally taking place with the extrication of light and heat. These alloys are much more fusible than pure platinum: care must therefore be taken not to heat the oxides of easily reduced metals, such as lead or bismuth, in platinum crucibles, as if the oxides should happen to be reduced, the crucible would be destroyed by the formation of a fusible alloy. Most of the platinum of commerce contains iridium, which, without impairing its power of resisting chemical agents, increases its hardness and durability. It is remarkable, that though pure platinum is perfectly insoluble in nitric acid, yet when alloyed with 10 or 12 times its weight of silver, both metals are easily and completely dissolved by it. An amalgam of platinum may be formed by acting upon an amalgam of sodium with a neutral solution of the double chloride of platinum and sodium; and, according to Levol, when this amalgam is attacked by nitric acid, the platinum as well as the mercury is partially dissolved.

Platinum enters into combination with carbon and with silicon: sometimes in the fusion of ordinary platinum wire before the blowpipe, the globules of the melted metal become covered with a film of colourless glass, arising from the oxidation of the silicon and the fusion of the resulting silica. A brittle granular compound of platinum and silicon was accidentally obtained by Daniell, owing to the action of silicon at a high temperature upon one of the platinum bars of his pyrometer. It appeared to be formed by a kind of cementation, the silicon being derived from the clay of the

envelope in which the bar was heated: the proportion of silicon amounted to 1·5 per cent. A fusible compound of platinum with boron was also obtained by Wöhler and Deville.

(825) OXIDES OF PLATINUM.—There are two oxides of platinum, a protoxide and a binoxide. The *protoxide* ($PtO = 106·5$) is procured by digesting the protochloride of the metal in a solution of potash: a dark-olive green liquid is thus obtained owing to the solution of the oxide in the excess of alkali. On neutralizing the solution with sulphuric acid, a black hydrated protoxide of platinum subsides. It is slowly dissolved by acids, forming unstable salts with them, and is readily decomposed by heat.

The *Binoxide* ($PtO_2 = 114·5$) has a strong tendency to combine with alkaline bases; it is therefore prepared by adding to a solution of nitrate of platinum only one half of the quantity of carbonate of soda which is necessary for its complete precipitation. It is thus procured as a voluminous brown hydrate ($PtO_2, 2\,HO$), from which water is expelled at a gentle heat, whilst the mass becomes darker; a higher temperature expels the whole of the oxygen. Hydrated oxide of platinum is soluble in solutions of potash and soda; the compounds thus formed may be obtained in crystals. The soda compound consists of ($NaO, 3\,PtO_2 + 6\,Aq$). Binoxide of platinum also enters into combination with other bases, forming compounds most of which are insoluble. The oxide is also soluble in acids, and forms well characterized salts, the solutions of which have a yellowish-brown colour.

(826) SULPHIDES OF PLATINUM.—Platinum combines with sulphur in two proportions, PtS and PtS_2.

The *protosulphide* (PtS) may be obtained as a black precipitate by passing sulphuretted hydrogen over moistened protochloride of platinum; it may also be procured by heating sulphur with the double chloride of platinum and ammonium, when it assumes the form of a grey powder of metallic appearance, from which the sulphur is completely expelled by heating it in the open air.

The *Bisulphide* (PtS_2) is best procured by decomposing the double chloride of sodium and platinum by sulphuretted hydrogen; it falls as a dark-brown powder, which becomes black during desiccation. It is somewhat soluble in the sulphides of the alkaline metals. By ignition in closed vessels it is converted into protosulphide. When exposed to the air, and gently heated, it is partially converted into sulphate, but at a higher temperature is wholly decomposed, metallic platinum remaining.

(827) CHLORIDES OF PLATINUM.—These correspond in number and composition to the sulphides and oxides of the metal.

In order to procure the *protochloride* ($PtCl = 134$), the solution of platinum in aqua regia should be evaporated, and the residue exposed to a heat of 450°, so long as any chlorine is expelled; the compound which remains is the protochloride. It is of an olive colour, and is insoluble in water: it is scarcely acted upon by nitric or by sulphuric acid; hydrochloric acid dissolves it sparingly: but it is dissolved easily by caustic potash, and by the bichloride of platinum, with which latter it forms a double salt, of so deep a brown colour as to appear opaque in a concentrated solution. It forms crystallizable double salts with the chlorides of the alkaline metals.

Bichloride of Platinum ($PtCl_2 = 169.5$) is obtained by dissolving platinum in aqua regia, and evaporating the solution to dryness by means of a steam heat.* It is a deliquescent salt, and forms a deep orange-coloured solution in water, from which it may be obtained crystallized in prisms; it is also dissolved largely by alcohol and by ether. When heated to 450° it loses half its chlorine, forming the protochloride, and if the temperature be further raised, it is completely decomposed, and metallic platinum is left.

With other chlorides it forms numerous double salts, which are produced by mixing the solutions of these chlorides with that of the bichloride of platinum, and evaporating. The *double chloride with potassium* ($KCl,PtCl_2 = 244$) is a sparingly soluble anhydrous compound, which crystallizes in octohedra; it is insoluble in alcohol and in ether. This salt is commonly used as a means of determining analytically the quantity of potash in a compound. It is decomposed by a red heat, into chloride of potassium and metallic platinum. The double *chloride of platinum and sodium* ($NaCl,PtCl_2 + 6\,Aq$) crystallizes in beautiful red striated prisms, which are soluble in water, alcohol, and ether. With *chloride of ammonium* a compound is formed ($H_4NCl,PtCl_2 = 222$) very similar in appearance to that with potassium, with which it is isomorphous: it is sparingly soluble in water, and is insoluble in alcohol and in ether. This salt is employed in analysis for determining the

* In an active laboratory a number of residues containing platinum gradually accumulate, and these may be turned to account in the following manner:—The solutions, mixed with the precipitates, are evaporated to dryness, and transferred to a clay crucible in which they are heated strongly, with free access of air, in order to burn off organic matters; after which the residue is boiled with hydrochloric acid, then with water, and lastly with nitric acid; a thorough washing with water follows. The impurities having thus been removed, the residual platinum may be converted into bichloride by means of aqua regia.

quantity of ammonia present in solutions. It is also made use of for separating platinum from the other metals with which it is associated, after they have been brought into solution by treating the ore with aqua regia (821). When the chloride of platinum and ammonium is ignited, the ammonium and chlorine are wholly expelled, and pure platinum remains in the spongy form.

(828) *Basic Ammoniacal derivatives from the Chloride of Platinum.*—The action of ammonia upon the protochloride of platinum gives rise to the formation of several remarkable compound bases, the composition of which offers considerable interest in a theoretical point of view. Magnus found that if the protochloride of platinum be dissolved in hydrochloric acid, the addition of an excess of ammonia to the boiling solution causes the deposition of brilliant, green, acicular crystals which are insoluble in water and in hydrochloric acid: they contain the elements of 2 atoms of protochloride of platinum, and 2 of ammonia ($Pt_2Cl_2H_6N_2$). This compound, however, undergoes no change when digested at ordinary temperatures in solutions of the caustic alkalies, or in the concentrated acids, but when boiled with them it is slowly decomposed. If digested in nitric acid, one half of the platinum is separated in the metallic state, and on evaporating the solution, a salt is obtained crystallized in small flattened prisms ($PtClH_6N_2O,NO_5$). Neither the chlorine nor the platinum can be detected in this solution by the usual tests. The nitric acid may be displaced from it by double decomposition with sulphate, phosphate, or oxalate of soda, and a sparingly soluble sulphate, phosphate, or oxalate of the base is then formed. The base of these salts (commonly called *Gros's salts,* from the name of their discoverer) has not been isolated.

Raewsky discovered that if the green salt of Magnus be boiled with an excess of nitric acid, red fumes are disengaged, and a different salt is formed, which may be obtained in crystals on evaporation. The nitric acid may be displaced from this compound by an equivalent quantity of oxalic or of carbonic acid.

Besides these compounds, other platinum bases derived from ammonia have been obtained, of which the following is a brief account.

Platosamine; Reiset's second base (PtH_3NO).—This is a greyish mass insoluble in water and in ammonia, which may be obtained by heating the hydrate of diplatosamine (PtH_6N_2O,HO) to 230°, so long as it gives off water and ammonia. It combines with acids, and forms salts, most of which are insoluble, and

detonate on the application of heat. Chloride of platosamine (PtH_3NCl) may be obtained by heating the chloride of the following base, so long as it gives off water and ammonia.

Diplatosamine ; Reiset's first base ($PtH_6N_2O + HO$).—This substance may be procured as a hydrate in deliquescent needles, which are powerfully alkaline, caustic, and absorb carbonic acid from the air. It is usually isolated by decomposing its sulphate by its exact equivalent of hydrate of baryta. In order to prepare its salts the green compound of Magnus ($Pt_2Cl_2H_6N_2$) is brought into solution by boiling it for some hours with a solution of caustic ammonia, when the chloride of diplatosamine ($PtH_6N_2Cl + HO$) is formed in the liquid and crystallizes easily. If a solution of this salt be decomposed with an equivalent of sulphate of silver, the sulphate of diplatosamine is obtained, and may readily be procured in crystals; the nitrate may be obtained by similar means.

Platinamine; Gerhardt's base (PtH_3NO_2).—This compound may be obtained in the form of striated very brilliant rhomboidal prisms of a yellowish colour. It is nearly insoluble in boiling water, is not decomposed by a boiling solution of potash, but is readily dissolved by diluted acids, and forms a large number of crystallizable, sparingly soluble salts, which are of a yellowish colour. Some of these salts are neutral, and some are acid. Platinamine is usually obtained by adding ammonia to a boiling solution of the neutral nitrate. If chloride of platosamine be suspended in boiling water, and submitted to a current of chlorine, the elements of ammonia are removed, and it is slowly transformed into bichloride of platinamine (PtH_3NCl_2), and this by long boiling with nitrate of silver is converted into the nitrate of platinamine ($PtH_3NO_2,NO_5,3\ HO$).

Diplatinamine is supposed by Gerhardt to be the base of the salts of Gros and of Raewsky; but it has not as yet been isolated.

The following table contains the formulæ of the principal series of these compounds which have been ascertained to exist :*—

1. *Salts of Platosamine* (Reiset's second base).

Platosamine	PtH_3NO.
Hydrochlorate of platosamine (yellow)	PtH_3NCl.
Nitrate of platosamine	PtH_3NO,NO_5.

* The following papers may be consulted upon this subject: Gros, *Ann. de Chimie*, II. lxix. 204; Reiset, *Ib.*, III. xi. 417; Raewsky, *Ib.*, III. xxii. 278; Peyrone, *Liebig's Annal.*, li. 1, and lv. 205; Gerhardt, *Comptes Rendus des travaux de Chimie*, par Laurent et Gerhardt, 1849, p. 113, and 1850, p. 273; Buckton, *Q. J. Chem. Soc.* v. 213, and vii. 22.

2. *Salts of Diplatosamine* (Reiset's first base).

Diplatosamine (hydrate of) . . .	$PtH_6N_2,O+HO$.
Hydrochlorate of diplatosamine . .	$PtH_6N_2,Cl+HO$.
Magnus's green salt	$PtH_6N_2Cl,PtCl$.
Nitrate of diplatosamine	PtH_6N_2O,NO_5.
Bicarbonate of diplatosamine . .	$HO,PtH_6N_2O, 2\ CO_2$.

3. *Salts of Platinamine* (Gerhardt's base).

Platinamine	PtH_3NO_2.
Bihydrochlorate of platinamine . . .	PtH_3NCl_2.
Neutral nitrate of platinamine . .	$PtH_3NO_2,NO_5\ 3\ HO$.
Binitrate	$PtH_3NO_2, 2\ NO_5$.

4. *Salts of Diplatinamine.*

Diplatinamine (not isolated) . . .	$PtH_6N_2O_2$.
Hydrochlorate of diplatinamine . .	PtH_5N_2Cl.
Neutral nitrate	$PtH_6N_2O_2,NO_5, HO$.
Sesquinitrate	$2\ (PtH_6N_2O_2), 3\ NO_5,HO$.

5. *Salts obtained by Gros.*

Base (not isolated)	$PtClH_6N_2O$.
Hydrochlorate	$PtClH_6N_2Cl$.
(viewed by Gerhardt as bihydrochlorate of diplatinamine)	$PtH_6N_2Cl_2$.
Nitrate	$PtClH_6N_2O,NO_5$.

6. *Salts obtained by Raewsky.**

Base (not isolated)	
Binitrate (crystallized)	$Pt_2ClH_{12}N_4O_5, 2\ NO_5$.
Phosphate	$Pt_2ClH_{12}N_4O_5,PO_5,HO$.
Bicarbonate	$Pt_2ClH_{12}N_4O_5, 2\ CO_2$.

(829) The *Bibromide of Platinum* is a brown insoluble powder.

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* Gerhardt disputes the correctness of Raewsky's formulæ, which are certainly very complicated and improbable: he found these compounds to contain 2 atoms less of oxygen, and regards the salts discovered by Raewsky as sesquiacid salts of diplatinamine, and he views those of Gros as biacid salts of diplatinamine, in some of which two acids are present. But a serious objection to this theory of Gros's salts, is afforded by the fact that Gros's hydrochlorate abandons only half its chlorine when mixed with the solution of nitrate of silver. It ought to give up the whole were Gerhardt's hypothesis correct.

A very ingenious theory of the composition of the first four bases has been proposed by the same chemist. He supposes platinum, in common with several other metals (such as mercury, iron, palladium, and cobalt), to have

A *Biniodide of Platinum* is precipitated as a sparingly soluble powder of a deep wine-red colour, on adding iodide of potassium to a dilute solution of bichloride of platinum.

Fulminating platinum ($Pt_3HNO_2+4\,Aq=(\frac{1}{2}\,Pt)_4N,O,HO+4\,Aq$; Gerhardt) is procured as an insoluble black powder by dissolving the chloride of platinum and ammonium in a solution of caustic soda and adding an excess of acetic acid, or by precipitating the sulphate with an excess of ammonia. It may be regarded as a hydrated oxide of ammonium in which the 4 atoms of hydrogen have been displaced by two atoms of platinum, or by 4 equivalents of *platinicum*. Hydrochloric acid dissolves this compound, forming with it a very soluble, uncrystallizable salt: other acids decompose it with formation of ammoniacal salts. If suddenly heated to about 400° it explodes.

The *persulphate* of platinum may be formed by treating the bisulphide with fuming nitric acid, and heating, to expel the excess of nitric acid. The *pernitrate* may be formed by decomposing a solution of the persulphate by an equivalent quantity of the nitrate of baryta; both these salts yield insoluble double subsalts on the addition of an alkali.

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the power of entering into combination with two different proportional numbers; one of these is the number 98·5, ordinarily assumed as the atomic weight of the metal (which he terms *platinosum*), having a symbol Pt. The other proportional is equal to one-half of this, or 49·8; and is termed *platinicum*, its symbol being pt, or ($\frac{1}{2}$ Pt). The compound usually known as protochloride of platinum (PtCl), Gerhardt terms *chloride of platinosum*; and the salt ordinarily described as bichloride of platinum $PtCl_2$, he designates as *chloride of platinicum* (ptCl) or ($\frac{1}{2}$ Pt,Cl).

The different platinum bases are viewed by Gerhardt as compound ammonias in which a portion of the hydrogen is displaced by platinum. The salts of platosamine, as well as those of diplatosamine, require 1 equivalent of a monobasic acid for their neutralization; they each contain 1 proportional of platinosum, this being the element which confers upon them their basic power. The salts of platinamine, and of diplatinamine, on the other hand, are supposed to contain 2 proportionals of platinicum; and thus the necessity for 2 equivalents of acid in order to neutralize these bases is explained. The following table, which represents the compounds formed by these different bases with hydrochloric acid, will illustrate this theory:—

Chlorides of Platinum Bases.	By Gerhardt's Theory.	Empirical Formula.
Hydrochlorate of Platosamine . .	PtH_2N,HCl . .	PtH_3NCl.
——— Diplatosamine .	PtH_5N_2,HCl . .	PtH_6N_2Cl.
——— Platinamine . .	$(\frac{1}{2}\,Pt)_2HN,2\,HCl$.	PtH_3NCl_2.
——— Diplatinamine .	$(\frac{1}{2}\,Pt)_2H_4N_2,2\,HCl$	$PtH_6N_2Cl_2$.

This theory of the existence of two different equivalents of platinum adapts itself very happily to the case which we are now considering, but when the attempt is made to generalize it, by assuming that iron, copper, &c., also have two different equivalents, it is open to very serious objections, which are fatal to its general adoption.

(830) CHARACTERS OF THE SALTS OF PLATINUM.—1. The *proto-salts* of platinum are unimportant.

2. Of the *persalts* of platinum the bichloride is the only soluble compound of frequent occurrence. These salts are distinguished by the following characters. When heated they are all decomposed, and leave a residue of metallic platinum. They have a brownish-yellow colour in solution: with *potash*, or with any of its salts, they give a yellow precipitate of the chloride of platinum and potassium, which is soluble in a large excess of caustic potash: *soda* precipitates a brown hydrated oxide which is soluble in excess of the alkali: with *ammonia*, or a soluble salt of ammonia, a yellow chloride of platinum and ammonium is precipitated, which is decomposed by heat, leaving metallic platinum. *Sulphuretted hydrogen* and *hydrosulphate of ammonia* give a black sulphide, which is soluble in a large excess of the sulphides of the alkaline metals.

Solutions of the salts of platinum are reduced by the *subnitrate of mercury*, but not by *protosulphate of iron*. *Protochloride of tin* produces a very deep brown solution, but yields no precipitate; *iodide of potassium* gives a brown precipitate of iodide of platinum. The solutions of the salts of platinum are readily reduced to the metallic state by means of *zinc* or *iron*. Oxalic acid exerts no reducing action upon the salts of platinum, which may thus be separated from those of gold; and after the gold has been precipitated in this manner, the platinum may be thrown down in the metallic form by boiling the liquid with a soluble formiate, taking care first to neutralize the liquid by the addition of carbonate of soda.

(831) *Estimation of Platinum.*—Platinum may be estimated either in the metallic state, or in the form of a double chloride of platinum with potassium or ammonium. The solutions from which these double salts are precipitated should be concentrated; the complete separation of the salt is favoured by the addition of alcohol, and the washing of the precipitate should be performed with dilute alcohol. Platinum may thus be separated from all the metals hitherto described: 100 parts of the double chloride of platinum and potassium contain 40·43 of the metal; and 100 parts of the ammoniacal salt contain 44·28 of platinum.

§ V. Palladium ($Pd=53 \cdot 24$). *Sp. Gr.* 11·4 to 11·8.

(832) Palladium is one of the rare metals which occur chiefly in the ore of platinum, in which it was discovered by Wollaston in the year 1803. It usually forms from 1 to $\frac{1}{3}$ per cent. of these ores. According to G. Rose, palladium is dimorphous, since it is found native in cubes, and in six-sided plates.

In order to extract the metal from the ore of platinum, the solution of this ore in aqua regia is treated with chloride of ammonium with a view to separate the platinum, as already described (821), and to the filtered liquid, cyanide of mercury in solution is added; a yellowish-white, flocculent cyanide of palladium subsides; this is converted into a sulphide by heating it in contact with sulphur, and the sulphur is subsequently expelled by repeated roastings. Another source of palladium is the native alloy which it forms with gold, and which is found in the Brazilian mines. In order to extract the palladium from it, Mr. Cock directs the alloy to be fused with silver, and then boiled in nitric acid, by which all the metals except the gold are brought into solution. The decanted liquid is next mixed with a solution of common salt, by which the whole of the silver is thrown down in the form of chloride, whilst the palladium with the other metals (which consist principally of copper with some lead and iron,) still remains dissolved. Bars of metallic zinc are then introduced into the liquid, and these metals are precipitated upon the zinc in the form of a black powder, consisting of reduced metal. This precipitate is washed and redissolved in nitric acid, supersaturated with ammonia, which dissolves the oxides of palladium and copper, while those of iron and lead are precipitated: the clear liquid is now supersaturated by hydrochloric acid. Palladium is thus thrown down in the form of a yellow, sparingly soluble, double chloride of palladium and ammonium; by ignition it is reduced, and agglutinates, but does not fuse. A small quantity of palladium still remains in solution, and may be recovered by the introduction of bars of iron.

Palladium is a white, hard metal possessed of considerable ductility and tenacity. It is not fusible in an ordinary wind furnace, but melts at a lower temperature than platinum. Deville and Debray state that, like silver, it absorbs oxygen when melted, and as the metal cools the globule spits. Before the oxyhydrogen blowpipe it burns with scintillation, and if heated on lime it is

slowly dispersed in green vapours. It undergoes no change in the open air at ordinary temperatures; but at a low red heat it becomes covered with an iridescent film, owing to a superficial oxidation; on increasing the heat, the oxygen is expelled, and the metal resumes its brilliant surface. Palladium is dissolved when heated in nitric acid, or in aqua regia, but it is acted upon by the other acids with difficulty. When fused either with bisulphate of potash, with nitre, or with the alkalies, it is oxidized. If a solution of iodine in alcohol be evaporated on a slip of palladium, a stain is left, by which this metal is at once distinguished from platinum. Palladium combines readily with gold, which is rendered brittle by its presence even in small proportion. It has a remarkable power of whitening the colour of gold, even though present in the mixture only in small quantity; and when it forms 20 per cent. of the mass, the alloy is quite white. If alloyed with twice its weight of silver it forms a ductile compound which is well adapted for the construction of small weights. When melted with 8 times its weight of tin, at a red heat, an alloy is formed (Pd_3Sn_2), which is obtained in beautiful brilliant lamellæ on digesting the mass when cold in hydrochloric acid. Palladium has been applied in a few cases to the construction of graduated scales for astronomical instruments, for which, by its whiteness, hardness, and inalterability in air, it is well adapted.

(833) Oxides of Palladium.—This metal appears to form three oxides: a protoxide, PdO, which is the base of the salts of the metal; a binoxide, PdO_2; and a suboxide, Pd_2O, which furnishes a series of salts resembling those of suboxide of copper, and which, according to Kane, is obtained by heating the hydrated protoxide to incipient redness.

The *protoxide* (PdO=61·2) may be procured as a black powder, by heating the nitrate to low redness; or it may be obtained upon adding carbonate of potash or soda to its salts, as a dark brown hydrate, soluble both in acids and in alkalies, and from which the water may be expelled by heat. At a bright red heat it loses its oxygen.

The *binoxide* (PdO_2) is prepared by decomposing the solid double chloride of palladium and potassium by a solution of potash; it forms a yellowish-brown hydrate, which obstinately retains a portion of alkali: it is soluble in the alkalies; by boiling it with water it is rendered anhydrous, and is then deposited as a black powder.

Sulphide of Palladium (PdS) may be formed either directly, by heating powdered sulphur with palladium, or by precipitating

the salts of the protoxide by means of sulphuretted hydrogen; it forms a fusible, greyish-white, lustrous mass, from which heat expels the sulphur.

If a piece of palladium foil or wire be held in the flame of a spirit lamp, soot is speedily deposited in large quantity, the foil or wire is corroded, and the mass of soot is found to contain palladium throughout, owing to the formation of a carbide of the metal.

(834) *Chloride of Palladium* (PdCl) is obtained by evaporating to dryness a solution of palladium in aqua regia; it forms brown hydrated crystals, which become black when the water is expelled; if heated to redness metallic palladium is left. Chloride of palladium forms double salts with the soluble chlorides; those with potassium and ammonium are yellow. With ammonia, chloride of palladium forms a series of compounds analogous to those of platinum (828): one of them, *palladamine* (PdH_3N)O, is a crystallizable powerfully alkaline base. The *bichloride* of palladium ($PdCl_2$) exists in solution in aqua regia, but cannot be obtained in crystals: it forms double salts with the chlorides of the alkaline metals; the double salt with potassium crystallizes in ruby-red prisms.

Iodide of Palladium (PdI = 180·2).—This compound is obtained by adding a solution of a salt of palladium in slight excess to one of iodide of potassium. It is a black powder, insoluble in water, but soluble in ammonia, and in a solution of iodide of potassium; a solution of palladium is sometimes employed as a precipitant for iodine when it is necessary to separate iodine from chlorine and bromine (446). Iodide of palladium loses its iodine when strongly heated.

Cyanogen has a stronger affinity for palladium than for any other metal. This *cyanide* is procured as a yellowish precipitate by adding cyanide of mercury or of potassium to neutral solutions of any of the salts of palladium; it is soluble in ammonia, in acids, and in cyanide of potassium; it forms a series of double cyanides.

The *Sulphate of Palladium* (PdO,SO_3) may be obtained by decomposing the nitrate by sulphuric acid, or by dissolving the oxide in sulphuric acid. It is a deliquescent salt which forms a deep brownish-red solution; when heated it loses acid, and furnishes a subsalt.

The *nitrate* is formed by boiling nitric acid on palladium: it may be obtained in rhomboidal prisms; they are freely soluble in a small quantity of water, and yield a deep reddish-brown liquid; but on being largely diluted the neutral salt is decomposed, and an insoluble basic nitrate is precipitated. If ammonia in excess be added to the solution of the nitrate, an ammoniacal nitrate of palladium may be crystallized from it in rectangular tables.

(835) Characters of the Salts of Palladium.—The proto-salts, or ordinary salts of palladium form either brown or red solutions, which when neutral are distinguished by the yellowish precipitate of cyanide of palladium, formed on adding *cyanide of mercury*. The fixed *alkalies* precipitate the compounds of palladium in the form of a red or orange subsalt, which is soluble in excess of the alkali by the aid of heat. *Ammonia* and its *carbonate*, when added to a solution of chloride of palladium, give a flesh-coloured precipitate, soluble in excess of ammonia. Nitrate of palladium gives a brown precipitate with ammonia. *Carbonates of potash* and *of soda*, yield a brown precipitate of the hydrated oxide, with salts of palladium. *Iodide of potassium* precipitates a black iodide of palladium. *Sulphuretted hydrogen* and *hydrosulphate of ammonia* throw down a black sulphide of palladium, insoluble in the sulphides of the alkaline metals. Solutions of the salts of palladium are reduced by a solution of *protosulphate of iron*, and by many of the metals, the reduction being facilitated by heat. *Protochloride of tin* produces a dark brown precipitate, which is soluble in hydrochloric acid, forming an intense green solution, which becomes reddish brown on dilution.

Palladium may be separated from all other metals, except copper and lead, by the addition of the cyanide of mercury to the solution previously neutralized by means of carbonate of soda. The cyanide of palladium when ignited in the air leaves metallic palladium.

§ VI. Rhodium (Ro=52·16). *Sp. Gr.* 12·1.

(836) Rhodium was discovered by Wollaston in 1803. It usually forms about one-half per cent. of the ore of platinum; it may be extracted from the solution of this ore in aqua regia after the platinum and palladium have been separated by the addition of sal ammoniac and cyanide of mercury: the excess of cyanide of mercury is then decomposed by acidulating the solution with hydrochloric acid, adding common salt, and evaporating to dryness; the chloride of sodium thus forms double chlorides with all the metals in solution; the residue is treated with alcohol (of sp. gr. 0·837), which dissolves all these double salts, except that of sodium and rhodium, which remains behind as a red powder; this is dissolved in water, and the rhodium thrown down in a pulverulent form by means of bars of metallic zinc. The chloride of sodium and rhodium may also be decomposed by heating it in a

current of hydrogen gas, when, on washing the mass with water, the rhodium is left in a pulverulent form.

Rhodium is a white, very hard metal; when quite pure, it is malleable after fusion upon lime, and it then has a sp. gr. of 12·1. It requires a stronger heat to fuse it than platinum, and when melted has a similar tendency to absorb oxygen and to spit as the globule sets.

Deville says that rhodium furnishes an alloy with platinum, which is easily worked; when the proportion of rhodium forms 30 per cent. or upwards of the alloy it is not attacked by aqua regia. When pure, rhodium is insoluble in the acids, though if alloyed in small quantity with platinum, copper, bismuth, or lead, it is dissolved with them in nitrohydrochloric acid. Rhodium has a considerable affinity for oxygen, and may be oxidized by fusion with a mixture of nitre and carbonate of potash; bisulphate of potash also oxidizes the metal and forms a soluble double sulphate of rhodium and potassium, whilst sulphurous acid escapes. If heated in contact with chloride of sodium, in a current of chlorine, a soluble double chloride of sodium and rhodium is produced.

(837) Oxides of Rhodium.—Rhodium has considerable affinity for oxygen: it appears to form two definite oxides, RoO and Ro_2O_3, besides some compounds intermediate between them. The *protoxide* has not been obtained in a state of purity.

Sesquioxide of Rhodium ($Ro_2O_3 = 128·3$).—This is the only salifiable oxide of rhodium; it may be procured by heating rhodium with a mixture of nitre and carbonate of potash; the oxide forms an insoluble compound with potash, which is to be well washed, and decomposed by digestion with hydrochloric acid: the sesquioxide is thus left as a greenish-grey hydrate which is insoluble in all acids.

Sulphides.—Rhodium forms two sulphides, RoS and Ro_2S_3.

If the metal be heated in the vapour of sulphur, the two bodies unite with incandescence, and form the *protosulphide*, which has a bluish-grey colour, and fuses at a very high temperature; the sulphur burns off in the open air and leaves a forgeable mass of metallic rhodium. The *sesquisulphide* may be obtained in the form of a brown hydrate by decomposing a hot solution of the double chloride of sodium and rhodium by means of sulphide of potassium or of sodium.

Chlorides of Rhodium.—Three of these, viz., RoCl; Ro_4Cl_6; and Ro_2Cl_3, are stated by Berzelius to exist, but the sesquichloride is the only one of importance.

Sesquichloride of rhodium is formed by decomposing the chlo-

ride of potassium and rhodium by silicofluoric acid, which separates the potassium as a gelatinous silicofluoride; the filtered liquid when evaporated to dryness, leaves the sesquichloride of rhodium. This chloride unites with many of the soluble chlorides to form crystallizable double salts, which are of a ruby or rose colour (whence the metal receives its name from ῥόδον, 'a rose'); that of sodium crystallizes in cubes or in octohedra, which are efflorescent in the air ($3\ NaCl, Ro_2Cl_3 + 18\ Aq$); they are insoluble in alcohol. When sesquichloride of rhodium is supersaturated with ammonia, the precipitate formed at first is redissolved, and a characteristic yellow compound, consisting of ($Ro_2Cl_3, 5\ H_3N$) is formed, by boiling, and may be purified by evaporation and re-crystallization. This compound when ignited leaves pure rhodium in the form of a powder.

(838) CHARACTERS OF THE SALTS OF RHODIUM.—The double chloride of sodium and rhodium is the best known of these compounds. The salts of the sesquioxide of the metal generally form rose-coloured solutions; they are decomposed by *iron* or *zinc*, which causes a deposit of metallic rhodium. *Potash* and *soda* slowly occasion a precipitate of yellow hydrated oxide, which obstinately retains a portion of the alkali; it is soluble in the excess of the alkali as well as in acids; if alcohol be added to the alkaline solution, a black precipitate gradually occurs without heat. *Iodide of potassium* throws down a sparingly soluble yellow iodide of rhodium. *Sulphuretted hydrogen*, when the solution is heated, slowly forms a brown precipitate insoluble in the alkaline sulphides. The *soluble sulphites* give a characteristic pale yellow precipitate. If the salts of rhodium be heated in a current of hydrogen, the metal is readily reduced: in this form it is insoluble in aqua regia, but if it be fused with bisulphate of potash the residue becomes soluble in water with a pink colour.

§ VII. RUTHENIUM (Ru=52·11). *Sp. Gr.*, from 11 to 11·4.

(839) *Treatment of the Platinum residue.*—After the platinum ore has been exhausted with aqua regia, a residue is obtained which frequently contains both titaniferous iron and chrome iron; but its most important constituent is an alloy in flat plates or scales, of a white colour and metallic lustre. This was formerly considered to be an alloy of osmium and iridium. It has, however, been found to consist of four metals—viz., osmium, iridium, ruthenium, and a small quantity of rhodium.

Fremy in separating the different metals contained in this residue avails himself of the oxidability of osmium and the volati-

lity of its peroxide. His process is the following:—About 3000 grains of the platinum residue placed in a porcelain or platinum tube, and heated to redness, is roasted in a current of dry air; in the portion of the tube which projects from the furnace some fragments of porcelain are placed, and the tube is connected with a series of glass flasks for the purpose of condensing the osmic acid as it distils; in the last flask a solution of potash is placed, in order to retain such portions of osmic acid as may have escaped condensation; and this flask is connected with an aspirator, by means of which a current of atmospheric air is maintained through the apparatus. The air is dried, and freed from organic particles before it enters the heated tube, by causing it to pass through tubes filled with pumice moistened with sulphuric acid. During the operation the osmium and ruthenium become oxidized; the osmic acid condenses in beautiful needles in the flasks, and mechanically carries forward the oxide of ruthenium, which is deposited upon the fragments of porcelain in regular crystals.*

The fixed residue consists of an alloy of iridium and rhodium, mixed with a little osmium and ruthenium. This is to be fused with caustic potash, by which the oxide of ruthenium is removed and is dissolved out on washing the fused mass with water. The undissolved portion is ignited with four times its weight of nitrate of potash, and the product is treated with boiling water, which dissolves the osmium, and on cooling, often deposits it in octohedral crystals of osmite of potash. The residue now contains only sesquioxides of iridium and of rhodium in combination with potash. Aqua regia, when boiled upon it, converts most of the iridium into the soluble bichloride; a solution of chloride of potassium is added to the liquid, after which crystals of the double chloride of iridium and potassium are deposited as it cools. The sesquioxide of rhodium, which is left undissolved, since it is insoluble in aqua regia, is converted into a soluble double salt by mixing it intimately with an equal weight of chloride of sodium, and heating the mass to dull redness in a current of dry chlorine.

(840) RUTHENIUM is a metal which, in 1845, was shown by Claus to exist in the ore of platinum. It is very hard, and brittle, and is scarcely fusible even before the oxyhydrogen blowpipe. The melted metal, according to Deville and Debray, has a sp. gr. of

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* Sometimes the osmide of iridium does not readily undergo oxidation. In such a case Deville fuses it with 8 or 10 times its weight of zinc, and heats it for some hours to full redness, he then dissolves out the zinc by hydrochloric acid, which leaves the platinum metals, in the form of a fine black powder, which is very easily oxidized in a current of air.

from 11 to 11·4. It absorbs oxygen at a red heat, and the oxide so obtained is not decomposed by simple elevation of temperature. The metal is readily oxidized by fusion with nitre, or with caustic potash. Ruthenium accompanies the alloy of osmium and iridium in a proportion varying from 3 to 6 per cent.; but it is not found in the portion of platinum ore which is soluble in aqua regia. It is most easily obtained by Fremy's process (839). The binoxide of ruthenium is not volatile when heated alone, but is carried forward mechanically by the peroxide of osmium, and becomes condensed in crystals near to the source of heat. By heating this oxide in a current of hydrogen, the metal is obtained in the form of a dark grey powder. The metal forms an alloy with tin, $RuSn_2$, which crystallizes in cubes of perfect regularity.

Ruthenium forms four compounds with oxygen, RuO; Ru_2O_3; RuO_2; and RuO_3.

Ruthenic acid (RuO_3) is an insoluble metallic acid; it may be obtained by heating any of the preceding oxides with nitre; the rutheniate of potash forms an orange-yellow solution in water. The *sesquioxide* is the most stable of the oxides of the metal; it is obtained in the anhydrous form by igniting the metal in a current of air. It is insoluble in the alkalies; but with acids it forms soluble salts which have a yellow colour. The alkalies precipitate the hydrated oxide ($Ru_2O_3,3HO$) from these solutions as a bulky blackish-brown powder.

There are three chlorides of ruthenium, $RuCl$; Ru_2Cl_3; and $RuCl_2$. The *sesquichloride* is obtained by dissolving the sesquioxide in hydrochloric acid: on evaporation it yields a greenish blue deliquescent mass, which is soluble in alcohol. *Sulphuretted hydrogen* causes a brown precipitate of sulphide of ruthenium in solutions of the sesquichloride, leaving a supernatant liquid of a fine blue colour, probably owing to the formation of protochloride of the metal; this reaction is very delicate, and characteristic of ruthenium. Metallic *zinc* also reduces the yellow sesquichloride to the blue protochloride, and ultimately precipitates the metal as a black powder. *Formiate* or *oxalate of soda*, if boiled with salts of ruthenium, renders the solution colourless, but does not occasion any precipitate of reduced metal. With *acetate of lead* a purplish red characteristic precipitate is formed. *Cyanide of mercury* renders the solution blue, whilst a blue precipitate is formed. The *caustic* and *carbonated alkalies* yield a black precipitate of the sesquioxide, insoluble in excess of the precipitant.

§ VIII. Osmium ($Os=99{\cdot}41$). *Sp. Gr.* 21·4.

(841) Osmium occurs associated with platinum in the form of an alloy of osmium, iridium, and ruthenium. It was discovered in the ore of platinum by Tennant, in 1803. Osmium may be obtained in the metallic condition by several processes. One of the simplest consists in treating osmic acid (OsO_4) obtained by Fremy's method (839) with hydrochloric acid and metallic mercury. Calomel is thus produced by the decomposition of the suboxide of mercury, which is formed at the expense of the oxygen contained in the oxide of osmium; $OsO_4+8\,Hg+4\,HCl=Os+4\,(Hg_2Cl)+4\,HO$. The water and the superfluous acid are expelled by evaporation to dryness, and on heating the residue in a small porcelain retort, the excess of mercury and calomel are driven off, leaving pure osmium in a pulverulent form. In this finely divided state, it emits the odour of osmic acid when exposed to a moist atmosphere; it takes fire when heated in the open air, and is dissolved by strong nitric acid, or by aqua regia, being converted into osmic acid. After ignition, however, it is no longer soluble in the acids. The specific gravity of osmium in the pulverulent form is about 10, but after it has been heated to the fusing point of rhodium in the oxyhydrogen jet it acquires a sp. gr. of 21·4 In order to obtain compact osmium, Deville and Debray oxidize the alloy of osmium and iridium by mixing it intimately with $5\frac{1}{2}$ times its weight of peroxide of barium, heating it to a bright red for 2 hours, after which they distil with a mixture of eight parts of hydrochloric and one of nitric acid. The osmic acid which passes over, is received into a solution of ammonia, supersaturated with sulphuretted hydrogen, and boiled. The sulphide of osmium is separated by filtration, dried at a low temperature, placed in a crucible of gas coke, which is enclosed in a clay crucible and luted down, then exposed for 4 or 5 hours to a heat sufficient to melt nickel. The osmium is reduced, and furnishes a brittle mass, the colour of which has more of a bluish cast than that of zinc. At a still higher temperature in the oxyhydrogen jet, at the fusing point of rhodium it becomes still denser. It may be heated in this condition to the fusing point of zinc without emitting vapour, but it takes fire at a higher temperature. If heated with 7 or 8 times its weight of tin in a charcoal crucible to a full red heat, the osmium is dissolved by the tin, and crystallizes out on slow cooling. On treating the mass with hydrochloric acid, the osmium is left as very hard crystalline powder. It may also be combined with zinc,

and on dissolving the zinc in hydrochloric acid the osmium is left as an amorphous combustible powder. Osmium appears to be the least fusible of the metals. In the oxyhydrogen jet platinum is volatilized, and iridium and ruthenium undergo fusion, but osmium does not melt, though it is volatilized by the intense heat.

Osmium differs remarkably from the other metals of this group, and presents more analogy with arsenic and antimony than with the noble metals.

(842) Five Oxides of Osmium are known;—OsO; Os_2O_3; OsO_2; OsO_3; OsO_4. The *protoxide* is of a dark green colour, it is soluble in acids, and forms green salts. The *sesquioxide* has not been isolated; it forms yellow uncrystallizable salts. The *binoxide* is black. The *teroxide* possesses the characters of a weak acid; it cannot be isolated, but it forms a crystalline compound with potash ($KO,OsO_3 + 2\,Aq$) which is sparingly soluble. This compound furnishes a good source of pure osmium. It is easily obtained by the addition of a little alcohol to a solution of the peroxide of osmium in potash; the osmite separates in large rose-coloured octohedra, which are permanent in a dry air, but absorb oxygen if moist. *Osmic acid* (OsO_4 *Comb. Vol.* 2; *Sp. Gr. of Vapour* 8·88) is the volatile compound which is produced when the metal is heated with nitre, or when roasted in air; it forms colourless, acicular, transparent, flexible crystals which are readily fusible, and are freely soluble in water; it boils at about 212°, emitting an extremely irritating and deleterious vapour, with a pungent characteristic odour somewhat resembling that of chlorine: hence the name of the metal osmium (from ὀσμὴ, 'odour'): it does not combine with acids; but though it unites with the alkalies, its solution does not redden litmus. It produces a permanent black stain upon the skin when touched, owing to the partial reduction of the metal, and gives a characteristic blue precipitate when its solutions are mixed with tincture of galls. If the solution of osmic acid be mixed with muriate of ammonia, a yellow sparingly soluble salt is formed (H_4NCl,OsO_2H_2N), which, when ignited in a current of hydrogen, leaves pure osmium. According to Fremy another oxide of osmium (OsO_5 ?) exists, but it is very unstable; it forms compounds with potash and soda which have a dark brown colour; they sometimes crystallize from concentrated alkaline solutions.

If the aqueous solution of osmic acid be treated with sulphuretted hydrogen, an immediate precipitate of the black hydrated *quadrisulphide* occurs, which is slightly soluble in solutions of the sulphides of the alkaline metals. Four inferior degrees of sulphu-

ration of osmium also exist; they correspond in composition with the oxides. These sulphides are decomposed by prolonged ignition, and pure osmium is left.

(843) There are four *chlorides of osmium*, viz.—$OsCl$; Os_2Cl_3; $OsCl_2$; $OsCl_3$: the *protochloride* is green, and sublimes in green needles; it is produced by heating powdered osmium in a current of chlorine; the double salts which it forms are of a green colour. The *bichloride* is formed in the same way as the protochloride, by employing an excess of chlorine; it is more volatile, and condenses as a red, crystalline, fusible, deliquescent powder: both this and the preceding chloride are dissolved by water, which soon decomposes them, forming osmic and hydrochloric acids, and depositing metallic osmium. The bichloride forms with chloride of potassium a beautiful sparingly soluble red salt, which furnishes octohedral crystals ($KCl,OsCl_2$); this salt is obtained by heating a mixture of osmium with chloride of potassium in a current of chlorine: it is isomorphous with the corresponding platinum salt, and yields a characteristic dark olive-green precipitate with nitrate of silver. Subnitrate of mercury gives with it a reddish-brown precipitate: tannic acid gives with it, when heated, a dark blue solution, and ferrocyanide of potassium, a chrome green liquid, passing into dark blue.

Double salts may also be formed which contain both a sesquichloride and a terchloride of osmium.

A compound of nitrogen, oxygen, and osmium (OsN,OsO_4), was formed by Fritsche and Struve. It may be obtained by acting upon a mixture of caustic potash and ammonia by means of osmic acid; these chemists termed it *osman-osmic acid*. With the alkalies it forms yellow crystalline compounds, which detonate readily when they are struck or suddenly heated.

The properties of the salts of osmium have been but incompletely ascertained. When boiled with nitric acid they all evolve vapours of peroxide of osmium.

§ IX. Iridium ($Ir=98{\cdot}56$). *Sp. Gr.* 21·15.

(844) Iridium was discovered at the same time as osmium by Smithson Tennant. It is occasionally found native and nearly pure in considerable masses among the Uralian ores of platinum, but it usually occurs combined with osmium as an alloy in flat scales. Iridium appears to be dimorphous, for it is found crystallized both in cubes and in double six-sided pyramids (G. Rose). In order to obtain the metal in the separate state, Wöhler recom-

mends the powdered alloy to be intimately mixed with an equal weight of finely powdered fused chloride of sodium, and the mixture to be heated to dull redness in a glass tube through which a current of dry chlorine is transmitted so long as it is absorbed. The alloy is decomposed by the chlorine; double chlorides of iridium and sodium, and of osmium and sodium are thus formed. They are dissolved in boiling water, and are thus freed from the insoluble portions. The solution is then concentrated, and the liquid so obtained is mixed with nitric acid and distilled; the double salt of osmium is decomposed by this means, and osmic acid is formed, whilst the iridium salt remains in the liquid: the osmic acid, being volatile, is expelled during the distillation. The addition of muriate of ammonia to the concentrated solution in the retort produces a precipitate of the double chloride of iridium and ammonium, which, upon ignition, yields metallic iridium. The metal, however, if obtained thus, is liable to be contaminated with ruthenium. It is preferable to adopt Fremy's method of procuring the double chloride of iridium and potassium (839). The salt may be decomposed by ignition in a current of hydrogen; and the chloride of potassium may be removed by washing with water, when the iridium is left in the form of a finely divided powder.

Iridium is a very hard, white, brittle metal, which may be melted on lime by the oxyhydrogen blowpipe, and by the heat of the voltaic current. It was found to have in its fused condition a density of 21·15 (Deville and Debray); and a native alloy of platinum and iridium even of sp. gr. 22·6 is known. If heated in a finely divided state in the open air it absorbs oxygen, but if in mass it remains unchanged by exposure to heat. In its isolated form it is unacted on by any of the acids or by aqua regia; but when alloyed with platinum it is readily dissolved by aqua regia. Pulverulent iridium, when fused with nitre or with the alkalies, becomes oxidized, and a similar effect is produced by heating it with bisulphate of potash. Iridium may be obtained in a finely divided state by decomposing a solution of its sulphate by alcohol: it then forms a black powder, which possesses properties similar to those of platinum black (823).

(845) Oxides of Iridium.—This metal forms three distinct combinations with oxygen, IrO; Ir_2O_3; and IrO_2: they pass readily one into the other, and thus give the variety of tints which solutions of the salts of this metal assume. From these changes of colour the name of iridium, derived from *Iris*, the rainbow, was conferred on the metal.

The *protoxide* is obtained as a black anhydrous powder by

decomposing the dry protochloride by means of a concentrated solution of potash. It is attacked by acids with difficulty, but is dissolved by the alkalies; the solution in potash absorbs oxygen from the air, and becomes blue. Its solutions in the acids have a dingy green colour.

The *sesquioxide* is the compound formed when iridium is fused with potash or with nitre, or by heating the pulverulent metal in air. It is a bluish-black powder, which is decomposed by a full red heat, and is readily reduced by hydrogen and combustible substances. This anhydrous oxide is insoluble in acids, and even in fused bisulphate of potash. If a solution of sesquichloride of iridium be boiled with a solution of potash, oxygen is absorbed, and an indigo-blue precipitate, which is a hydrate of the *binoxide of iridium* ($IrO_2, 2HO$) is formed (Claus). It may be rendered anhydrous by a gentle heat. The binoxide is but slowly dissolved by acids: the hydrochloric solution is at first blue, it then becomes green, and, when heated, changes to reddish-brown, whilst bichloride of iridium is formed.

Three *sulphides* of iridium corresponding to the oxides may be prepared by decomposing the chlorides of the metal by means of sulphuretted hydrogen.

Iridium, like palladium, when held in the flame of a spirit-lamp, becomes covered with carbonaceous excrescences, which contain a considerable portion of metallic iridium.

(846) CHLORIDES OF IRIDIUM.—These correspond in number and composition with the oxides. They all form double salts with the chlorides of the alkaline metals. The *protochloride* ($IrCl$) may be obtained by passing a current of chlorine over pulverulent iridium at a dull red heat: it forms an olive-green powder, insoluble in water, and nearly insoluble in hydrochloric acid (Berzelius). The *sesquichloride* (Ir_2Cl_3) is the most stable of the three chlorides; with subnitrate of mercury it gives a bright ochre-yellow precipitate ($Ir_2Cl_3 + 3\ Hg_2Cl$), and a similar compound is formed with nitrate of silver, which at first is dark blue, but soon becomes colourless: it forms salts with chloride of sodium and with chloride of potassium. If dry chlorine be transmitted over a mixture of finely divided iridium and chloride of potassium, a double salt, of a reddish-black colour ($KCl, IrCl_2$), consisting of bichloride of iridium and chloride of potassium, is formed. It may be dissolved in boiling water, and is deposited in octohedra on evaporating the solution; it corresponds in composition to the platinum salt, with which it is isomorphous. A similar salt of sodium may be formed in the same manner, by

substituting chloride of sodium for chloride of potassium: it is freely soluble. Bichloride of iridium forms a similar salt with sal-ammoniac, which possesses a very intense colouring power, and produces a dull brown solution even when much diluted. It is remarkable that the addition of potash in small quantity to this chloride converts it into the olive-green sesquichloride. Bichloride of iridium, when heated with ammonia, forms a series of compound bases analogous to those furnished by platinum and palladium.

Claus considers that the compounds formerly described as containing teroxide and terchloride of iridium were really compounds of ruthenium.

The salts of iridium have been but incompletely examined.

Iridium is apt to accompany the double chlorides of platinum with potassium and ammonium. It may be separated from platinum by precipitating the two metals together by means of chloride of potassium: the precipitate is washed, and either digested with cyanide of potassium which dissolves the iridium and leaves the platinum; or it may be fused with twice its weight of carbonate of potash. The platinum is by the latter operation reduced to the metallic state, whilst the iridium remains in the form of sesquioxide. The potash salts are removed by washing, and the platinum is redissolved by means of aqua regia, which does not attack the oxide of iridium. This operation sometimes requires repetition, as a portion of iridium may escape oxidation on the first occasion.

CHAPTER XVIII.

ON SOME CIRCUMSTANCES WHICH MODIFY THE OPERATIONS OF CHEMICAL AFFINITY.

(847) In the first part of this work an outline was given of the leading characters of the most important varieties of molecular and polar forces, as viewed in their simplest conditions. In the second portion of the work the attention of the reader has hitherto been directed principally to the results produced by the exertion of chemical affinity in the formation of the various compounds of inorganic origin, without reference to the effects of other forces which may have concurred in their production. It will, however, now be advisable to trace the influence exerted upon the operation of chemical affinity by the co-operation or antagonism of elasticity and cohesion, of adhesion, and of light, heat, and

electricity. Cases in which the chemical decomposition of one substance by another is due simply to differences in the degree of chemical affinity are much less numerous than might at first be imagined. The displacement of one metal by another from its solutions, such as that of silver by mercury, of mercury by copper, of copper by lead, and of lead by zinc (7, 5), furnishes some of the best examples of this kind; and similar instances are afforded by the displacement of one base by another insoluble base; as when oxide of copper is displaced from its combination with nitric acid by boiling it with freshly precipitated oxide of zinc, or oxide of silver.

§ I. Influence of Cohesion, Adhesion, and Elasticity.

(848) *Influence of Cohesion upon Affinity.*—Since chemical affinity is a molecular force, which is exerted only when the particles of bodies are within distances indefinitely small, minute subdivision and diminution of cohesion might be expected to favour its manifestation, by increasing the surfaces, and facilitating the mutual contact of the combining bodies. It will therefore be needless to give more than one or two instances in proof of this point. Iron, copper, lead, and many other metals, when exposed to the atmosphere in mass, are acted upon very slowly by it, and they gradually become converted into oxide upon the surface: if, however, they be reduced to a finely divided state, they are oxidized with such rapidity as often to become incandescent. If iron, cobalt, or nickel be reduced by hydrogen from its oxide, at a low red heat, it is obtained in this form: by the interposition of some infusible matter between the particles of the precipitated oxide, such, for example, as a little alumina or magnesia, the tendency to rapid oxidation is much increased; probably because the cohesion of the fine particles of reduced metal is mechanically prevented, and the access of the air to each portion takes place with facility. Copper, when precipitated from its solutions by metallic iron, or when reduced by means of hydrogen from its oxide at a low temperature, often takes fire and glows like tinder, when only a very slight elevation of temperature is applied to it. If a portion of tartrate of lead be exposed in a glass tube to a heat sufficient to char the acid, the metallic lead is reduced throughout the mass in a state of extreme division, and when poured into the air it generally takes fire, and burns with scintillations.

The opposite influence, exercised by the force of cohesion, is seen on contrasting the facility with which disintegrated carbon burns when in the shape of tinder, with the difficulty which is ex-

perienced in effecting the combustion of the compact coke which is deposited from coal gas upon the interior of the iron retorts; and a decrease of combustibility may be traced through all the different forms of carbon, in proportion as their hardness and density increase.

(849) *Influence of Adhesion and Solution on Affinity.*—It is mainly to the intimate subdivision effected by means of solution, that this operation owes its important influence in facilitating chemical combination. The force of cohesion amongst the component particles of the bodies dissolved is balanced by their adhesion to those of the liquid, and the particles of the substance in solution, being free to move in any direction, easily obey the force of affinity.

The influence of cohesion in preventing chemical action, and the manner in which the force of adhesion, as displayed in the production of solution, may act in favouring chemical action, are well exemplified by the effect of nitric acid upon carbonate of baryta. Nitrate of baryta, although soluble in water and in diluted nitric acid, is not soluble in the concentrated acid: when, therefore, concentrated nitric acid is poured upon finely powdered carbonate of baryta, it occasions but a slight effervescence, which speedily comes to an end, although the acid may be in large excess. If the liquid be diluted with a small quantity of water, a brisk effervescence is temporarily renewed, but again soon ceases; on a further addition of water, a fresh effervescence occurs, and when the acid has been diluted with 8 or 10 times its bulk of water, the whole of the carbonate of baryta is decomposed and dissolved.

For a similar reason, alcoholic solutions of acids are without action on the carbonates, unless the resulting salt be soluble in alcohol. A mixture of tartaric acid and alcohol will not decompose carbonate of potash. Hydrochloric acid when dissolved in alcohol will not decompose carbonate of potash, but will decompose carbonate of lime. An alcoholic solution of nitric acid decomposes carbonate of lime, but not carbonate of potash. The tartrates are insoluble in alcohol, so are chloride of potassium and nitrate of potash, but chloride of calcium and nitrate of lime are dissolved by alcohol freely.

(850) *Influence of Elasticity.*—In the numerous instances in which two salts produce mutual decomposition, frequent examples are afforded of the results produced by the interference of other forces with that of chemical affinity. The action of sulphate of ammonia on carbonate of lime is a case in point. If these two salts be mixed in a dry state, at ordinary temperatures, they do not

appear to act upon each other; but if subjected to the influence of a gentle heat, a double decomposition occurs, carbonate of ammonia and sulphate of lime are produced; the volatile carbonate of ammonia is expelled, and by the aid of the force of elasticity, it is removed from the mixture; $CaO,CO_2 + H_4NO,SO_3$ yielding $H_4NO,CO_2 + CaO,SO_3$. But suppose a solution of sulphate of lime to be mixed with one of carbonate of ammonia, the effects are exactly reversed; carbonate of lime, owing to its insolubility and the predominance of cohesion among its particles, is precipitated, whilst the soluble sulphate of ammonia remains in the liquid; and now $H_4NO,CO_2 + CaO,SO_3$ become $CaO,CO_2 + H_4NO,SO_3$. The chemist very often avails himself of the influence of elasticity in promoting chemical decomposition. When, for example, an acid is added to a salt, it may decompose that salt, and take the place of the acid previously in combination with the base, provided that the original acid can assume the gaseous form at ordinary temperatures, or can be converted into vapour, at a temperature below that required to volatilize the acid employed to displace it. Carbonic acid may thus be displaced from the carbonates by solutions of all the ordinary mineral and vegetable acids, except the hydrocyanic and hydrosulphuric acid.

It is upon this principle that sulphuric acid, when aided by heat, is employed to displace the nitric, the hydrochloric, the acetic, the formic, the butyric, and other volatile acids from their salts by distillation. Even a feebler but more fixed acid may expel the stronger acids which are more volatile than itself; thus oxalic acid, if boiled with solutions of the chlorides, expels hydrochloric acid from the liquid with facility.

A remarkable illustration of the important influence exerted by elasticity in counteracting powerful chemical affinities, is afforded in the decomposition of the sulphates themselves, by weaker acids at a high temperature:—for example, the affinity of sulphuric acid for bases is of the most energetic kind, whilst that of boracic acid, on the contrary, is extremely feeble. If a solution of borax be mixed with sulphuric acid, the soda of the salt will enter into combination with the sulphuric acid as it is added, and will gradually be separated from the boracic acid, which, if the liquid be hot and not too concentrated, is retained in solution. Owing to the peculiar action of boracic acid on blue litmus, it can be shown that the two acids do not divide the soda between them, for if a piece of blue litmus paper be placed in the liquid, it will exhibit the peculiar wine-red tint due to boracic acid, until a quantity of sulphuric acid exactly equivalent to the soda contained in the borax has been

added; but the moment that this point is reached, the least excess of sulphuric acid immediately reveals itself by the change of the colour of the litmus from dusky purplish-red to a bright red. It is therefore quite clear that boracic acid cannot effect even a partial displacement of sulphuric acid from its combination with soda when the two are in solution. But it is otherwise at a red heat: if boracic acid be fused with sulphate of soda, borax is produced, and sulphuric acid, which is volatile at this high temperature, is expelled in the elastic form. Other acids which are known to have a feebler affinity for bases than sulphuric acid, but which support a red heat without experiencing volatilization, such as the phosphoric and silicic acids, are also able to decompose the sulphates when heated with them.

In like manner when a base which is fixed is heated with the salt of a volatile base, the volatile base is displaced by the more fixed one; thus quicklime, or potash, if heated with the salts of ammonia, is converted into a salt of lime or of potash, whilst the ammonia escapes in the gaseous state.

(851) The effect of elasticity in removing from the sphere of action one of the components of a body which is undergoing decomposition, may in some cases be considerably assisted by mechanical means: and when the affinities of the displacing body, and of the substance displaced by it for the other constituent of the compound, are nearly equal, effects which are in apparent opposition to each other may sometimes be produced. For instance, oxide of iron, when heated to redness in a current of hydrogen gas, is gradually reduced to the metallic state:—the steps of the process appear to be these: a small quantity of water is formed; it immediately diffuses itself in vapour into the hydrogen, and is mechanically carried away by the current of this gas, which must be employed in considerable excess for this purpose; and this process goes on until the reduction is complete. On the other hand, if metallic iron be heated in a current of steam, water is decomposed, hydrogen is liberated, and is carried beyond the reach of chemical action upon the newly formed oxide of iron by the excess of the steam employed. In a similar manner, if a current of sulphuretted hydrogen be transmitted in large excess over solid bicarbonate of potash, aided by a gentle heat, the whole of the carbonic acid and water will be displaced from the bicarbonate, and carried forward by the excess of the gas, whilst sulphide of potassium will be formed. But sulphide of potassium, if dissolved in water, and subjected to a current of carbonic acid, will, in its turn, be gradually but completely decomposed; the sulphuretted hydrogen

being carried away by the excess of carbonic acid, whilst bicarbonate of potash is formed in the liquid.

(852) If elasticity be prevented by mechanical means from exerting its influence in removing a body from contact with others for which it has an affinity, combinations may be obtained, which cannot otherwise be procured. Wöhler (*Liebig's Annal.*, lxxxv. 376) found that a hydrate of sulphuretted hydrogen may be obtained in colourless crystals, if a portion of persulphide of hydrogen, freed from acid, be sealed up in a strong glass tube with a small quantity of water; the persulphide gradually undergoes decomposition into crystallized sulphur and gaseous sulphuretted hydrogen, which, at ordinary temperatures, exerts a pressure of about 17 atmospheres. Under these circumstances it combines with water, and forms a crystalline solid, which disappears with effervescence when the tube is heated to 86°, but is reproduced on cooling. If a tube containing crystals of this compound be opened, the crystals immediately disappear with brisk effervescence. In other cases, the decomposition of compounds already formed may be retarded or prevented, by preventing the escape of the elastic constituent by mechanical means. Hydrate of chlorine offers an instance of this kind. Under ordinary circumstances, this substance becomes liquid at a few degrees above the freezing point of water, with escape of gaseous chlorine; but if the solid hydrate be sealed up in a glass tube, it remains solid even when the temperature rises as high as 70°, the pressure of chlorine within the tube retarding the decomposition. Again, carbonate of lime is decomposed in an open fire, at a red heat, into carbonic acid and quicklime, but if it be enclosed in an iron tube, the mouth of which is plugged to prevent the escape of the acid, the carbonate may be melted, and on cooling it furnishes a granular mass, which is still carbonate of lime, and has the appearance of marble.

(853) *Action of Acids on Salts in Solution.*—Whenever an acid is added to a salt with the base of which it is capable of forming a soluble compound, it may be supposed to produce a division of the base between itself and the acid with which it was previously united, so that two acids and two salts may be present in the liquid, in some unknown proportions depending upon the strength of the relative affinities of the base for the two acids:—thus, when nitrate of potash is mixed with sulphuric acid, part of the potash may be supposed to enter into combination with the sulphuric acid, and part to remain united with the nitric acid, while a portion of nitric acid will be liberated, and will mix with the

uncombined sulphuric acid: thus, $2\,(HO,SO_3)+2\,(KO,NO_5)=KO,NO_5+KO,SO_3+HO,NO_5+HO,SO_3$. The occurrence of such a decomposition as this, although probable, in many cases does not admit of direct proof. If an additional force be called into operation, such as the development of elasticity on the application of heat, the more volatile acid may be expelled in the form of vapour, and may thus be withdrawn from the sphere of action. This, however, is no proof that such a partition of the base actually existed previous to the application of heat. In cases where the affinity of one acid for the base is very strong, whilst that of the other is feeble, the stronger acid may (as in the case of sulphuric acid and borax, already cited) entirely appropriate the base to itself. But where the two acids at all approach each other in chemical power, it must be assumed that a division of the base takes place. Sometimes the occurrence of such a partition can be proved by the change of colour which ensues after the mixture has been effected. Sulphate of copper, for example, is of a blue colour when in solution, and chloride of copper is green. If a solution of the blue sulphate be mixed with hydrochloric acid, it is evident that the oxide of copper enters partially into combination with the hydrochloric acid, since the solution assumes a bright green tint; $2\,(CuO,SO_3)+2\,HCl=CuO,SO_3+CuCl+HO,SO_3+HCl$.

If the base form an insoluble compound with the newly added acid, it is possible to decompose the original salt completely by its means. Thus, if a solution of nitrate or of acetate of baryta be mixed with sulphuric acid, it may be supposed that the baryta divides itself between the two acids in proportion to its affinity for each; but the sulphate of baryta being insoluble is at once withdrawn from the mixture, and the baryta remaining in the original salt again divides itself between the two acids: the fresh portion of sulphate of baryta, however, is immediately precipitated; and so, by a series of steps which, where the affinities are strong, succeed each other far more rapidly than they can be described,—the whole of the baryta is separated in the form of an insoluble sulphate, leaving the nitric or the acetic acid free in the solution.

A very feeble acid may even displace a more powerful one when the compound which it forms is insoluble in the menstruum in which it is suspended. Hydrocyanic acid will separate nitric acid from oxide of silver, owing to the formation of the insoluble cyanide of silver; $AgO,NO_5+HCy=HO,NO_5+AgCy$. Tartaric acid will liberate sulphuric acid in a solution of sulphate of silver, owing to the formation of an insoluble tartrate of silver. Oxalic acid will precipitate oxalate of copper from a solution of chloride

of copper; and Pelouze has observed that, if a current of carbonic acid be transmitted through a solution of acetate of potash dissolved in alcohol, acetic acid will be liberated, and carbonate of potash, which is insoluble in alcohol, will be separated; but no such change occurs in its aqueous solution, since carbonate of potash is freely soluble in water. This rule, however, is not without exception, where one acid is very powerful and the other is very feeble; borate of lime, for instance, is an insoluble salt, but a solution of boracic acid will not occasion any precipitate if mixed with one of nitrate of lime; citrate and tartrate of lime are also insoluble compounds, but neither solution of citric nor of tartaric acid occasions a precipitate in one of nitrate of lime.

In like manner, if the acid originally present be insoluble in water, it will be separated, and the salt will be decomposed; thus, on the addition of nitric acid to a solution of tungstate of potash, the tungstic acid is precipitated, whilst nitrate of potash is retained in the solution; $KO,WO_3+HO,NO_5=KO,NO_5+HO,WO_3$.

(854) *Action of Bases on Salts in Solution.*—An analogous decomposition occurs if a quantity of some additional base be added to a saline solution. If the two bases be soluble, and the salts which they form be also soluble, the solution will remain clear, and it may be supposed that the acid is divided between the two bases in proportion to its affinity for each, as when a solution of nitrate of baryta is mixed with a solution of potash: a mixture of nitrate of baryta and nitrate of potash with free baryta and free potash is thus obtained; but as baryta is less soluble than potash, a portion of the baryta will be gradually deposited if the solutions be in a concentrated form. If either of the bases be insoluble, or form an insoluble salt with the acid, a complete separation of the base or of the acid contained in the original salt may be effected. For example, the salts of nearly all the metals, with the exception of those of the alkalies and of the alkaline earths, contain as bases metallic oxides which are not soluble in water: the addition of any soluble base, such as potash, soda, or ammonia to their solutions, immediately occasions the precipitation of the insoluble oxide. It is in this manner that such oxides are commonly prepared from their solutions: for example, the oxide of zinc, of iron, of cobalt, of nickel, of manganese, or of silver, may thus be completely separated from the acid by which it was previously held in solution; thus, $CoO,SO_3+KO,HO=CoO,HO+KO,SO_3$. Solution of baryta, of strontia, or of lime, acts in a similar manner, if the acid is one which, like the nitric or the hydrochloric, is capable of forming a soluble compound

with these bases. A solution of nitrate of copper may thus be decomposed by a solution of baryta; $CuO,NO_5+BaO,HO=BaO,NO_5+CuO,HO$.

In a few cases no precipitation occurs even though the oxide be insoluble; thus, when cyanide of mercury is mixed with a solution of potash, no precipitate is produced, although oxide of mercury is insoluble in water.

If the newly added base form an insoluble compound with the acid, it is wholly precipitated by it; and if the other base be soluble, it remains in the liquid. One of the methods of forming a pure solution of potash is founded on this principle; in this experiment a solution of sulphate of potash is mixed with a quantity of solution of baryta exactly sufficient to precipitate the whole of the sulphuric acid; $KO,SO_3+BaO,HO=KO,HO+BaO,SO_3$; and in a similar manner oxalate of potash is deprived of its oxalic acid by the addition of lime-water to its solution, owing to the formation of an insoluble oxalate of lime. If the base as well as the salt which is formed by the addition of the new base to the acid be insoluble, it is possible to precipitate the whole of both acid and base from the liquid simultaneously; as when a solution of baryta is added in regulated quantities to a solution of sulphate of silver; $AgO,SO_3+BaO,HO=AgO,HO+BaO,SO_3$.

(855) *Mutual Action of Salts in Solution.*—It is a rule almost without exception,* *that when solutions of two salts, capable of forming by mutual interchange of acids and bases an insoluble or sparingly soluble salt, are mixed, the salts decompose each other, and the compound which is least soluble is precipitated.* It is in this manner that the greater number of insoluble compounds are formed by the process of double decomposition. Chloride of silver is thus obtained by acting upon a solution of nitrate of silver with one of common salt; $AgO,NO_5+NaCl=NaO,NO_5+AgCl$; and in a similar manner, if carbonate of manganese or phosphate of copper be required, it may be procured by mixing a solution of chloride of manganese or of sulphate of copper with one of carbonate of potash or of phosphate of soda. Sometimes a soluble compound may be advantageously procured in this manner, as in the ordinary method of preparing acetate of alumina, in which a solution of acetate of lead is mixed with one of sulphate of alumina: sulphate of lead is precipitated, and acetate of alumina remains

* When a solution of cyanide of mercury is mixed with one of nitrate of silver, little or no precipitate is produced, although cyanide of silver is a very insoluble compound, and cyanide of mercury has not the power of forming a soluble double cyanide with it.

dissolved; $3\ (PbO,C_4H_3O_3) + Al_2O_3, 3\ SO_3 = 3\ (PbO,SO_3) + Al_2O_3, 3\ C_4H_3O_3$.

When two saline solutions are mixed, which form, by the mutual interchange of their acids and bases, salts which are also freely soluble, in ordinary cases there is no proof that any change occurs, but it is usually supposed that a mixture of four different salts is produced. When, for instance, solutions of sulphate of potash and nitrate of soda are mingled, it is imagined that a mixture of sulphate of potash and sulphate of soda, of nitrate of potash and nitrate of soda, in unknown proportion, dependent upon the balance of the mutual affinities of the acids and bases, is the result. In like manner the mixture of three different acids and three different bases would occasion the formation of nine different salts; and the mixture of four salts, each containing different acids and different bases, should produce sixteen different salts, provided that all are capable of coexisting in solution.

Hence it will be seen that is impossible to state with certainty what are the salts which are present in mixture in any solution which contains a number of saline compounds. In the analysis of a mineral water, for example, it is possible to determine the amount of each acid and of each base which is present, but it is not possible to say what the salts really were which were brought into solution to form the mineral water in question. Sulphuric acid, nitric acid, carbonic acid, and chlorine may have been present amongst the acid constituents, and potash, soda, lime, and magnesia amongst the bases; but it is impossible to say how all those acids and bases are distributed in the solution. Many chemists allot the bases to the acids in the order of the insolubility of the different salts, whilst others allot the strongest bases to the strongest acids. In reporting the results of analysis, however, the quantities of the separate acids and bases should invariably be given; in addition to which, the analyst, if he pleases, can allot them according to his fancy. The foregoing remarks may be illustrated by the curious alternate decompositions which differences of solubility at different temperatures sometimes bring about; a striking instance of this kind occurs in the case of a mixture containing both sulphate of magnesia and common salt. These salts occur mixed together on a large scale in the mother-liquor of sea-water, after the bay-salt has been separated. Four salts may be formed by the intermixture of these two compounds, viz., sulphate of magnesia, sulphate of soda, chloride of magnesium, and chloride of sodium. Of these four salts, chloride of sodium is the least soluble at the boiling point; if, therefore, the solution be

concentrated by ebullition, chloride of sodium is separated in crystals; and as the liquid cools, the sulphate of magnesia crystallizes out. The effect, however, will be different if the solution be allowed to evaporate spontaneously in the open air; at low temperatures the sulphate of soda is the least soluble of the four salts; and at low temperatures it is the sulphate of soda which separates in crystals from the liquid, whilst the readily soluble chloride of magnesium remains in solution.

Upon a similar principle nitrate of soda is converted on a large scale into nitrate of potash, by mixing it with chloride of potassium; on concentrating the solution by boiling it, chloride of sodium is separated in crystals, and nitrate of potash crystallizes out as the liquid cools: at low temperatures chloride of sodium is more soluble than nitrate of potash, and the nitre crystallizes out nearly in a state of purity.

It may, in fact, be stated as a general principle, that on concentrating a mixed solution by evaporation, the salt which is least soluble at the particular temperature employed is that which is first formed.

In certain cases where there is no great difference in the solubility of two salts, evidence is afforded of their mutual decomposition when the solutions are mixed, by the change of colour which then ensues. Sulphocyanide of potassium, for example, when mixed with a solution of perchloride of iron, so much diluted as to be colourless, indicates, by the blood-red solution which it forms, that a mutual interchange of the components of the two salts has been partially effected. In like manner when a solution of protosulphate of iron is mixed with one of acetate of soda, a brown colour, similar to that of the acetate of iron, is produced; and further, on transmitting a current of sulphuretted hydrogen through the liquid, the iron is precipitated in the form of a black sulphide. This reaction could only take place owing to the presence of acetate of iron, since a solution of acetate of iron admits of being thus decomposed by sulphuretted hydrogen, but one of sulphate of iron is not so acted upon. The entire quantity of iron may be separated in this manner, for no sooner is a certain proportion of iron rendered insoluble, than a fresh portion of acetate of iron is formed; and this formation and decomposition of the salt continues as long as any iron remains in a state of solution.

(856) *Influence of Mass in the Formation of Chemical Compounds.*—A curious question presents itself as to the proportion in which two bodies are capable of thus mutually decomposing each other on mixture. When, for example, three different bodies, A, B,

and C, are mixed together, one of which, C, is capable of combining with either of the other two, and forming with them compounds, A C, B C, which in both cases are soluble, the quantity of A and of B being considerably in excess of C,—will the proportion in which C enters into combination with A and B, be determined merely by the strength of their relative affinities? or, will the proportion in which each of these bodies is present also influence the result? It was argued by Berthollet, that not only would C be divided between A and B, but that in proportion as the quantity of one of these bodies A, preponderated over the other body B, the proportion of A C in the mixture would be increased, while of course that of B C would be diminished. If, on the other hand, the proportion of B were increased, the quantity of the compound B C would be augmented, whilst that of A C would be proportionately lessened, the body C dividing itself between A and B, in a proportion represented by the product of its affinity for each of these elements multiplied into their mass. Thus if a represent the mass of A, let x represent its affinity for C, if β be the mass of B, and y its affinity for C; then A C : B C : : $ax : \beta y$. Suppose, for example, a solution of nitrate of potash to be mixed with more than its equivalent of sulphuric acid; it is generally conceded that the potash divides itself between the two acids, forming a mixture of sulphate and nitrate of potash, with free sulphuric and nitric acids. Now if the quantity of sulphuric acid be increased, will the quantity of sulphate of potash which is formed be influenced by the amount of sulphuric acid which is thus added in excess? and if so, to what extent will this influence of the *mass* of the acid modify the simple effect of chemical affinity.

Let us imagine for example, that x, the affinity of sulphuric acid for potash $= 5$, whilst y, that of nitric acid for potash $= 4$. When an equivalent of sulphuric acid is presented to an equivalent of nitrate of potash, the mass a of sulphuric acid $= 1$: that of the nitric acid $\beta = 1$ also. Then $ax : \beta y$ as $5 : 4$. The nitrate will be partially decomposed: $\frac{5}{9}$ of the potash will enter into combination with the sulphuric acid, whilst $\frac{4}{9}$ will be united with the nitric, and we shall have in the solution $\frac{5}{9}$ (KO,SO_3), $\frac{4}{9}$ (KO,NO_5) $\frac{4}{9}$ (HO,SO_3) and $\frac{5}{9}$ (HO,NO_5). But suppose, instead of adding 1 equivalent of sulphuric acid, 2 equivalents be employed, whilst the proportion of the nitrate remains unaltered; the mass a of the sulphuric acid is now 2, and $ax : \beta y$ as $10 : 4$. The proportion of nitrate of potash will be diminished, and there will be $\frac{10}{14}$ (KO,SO_3), $\frac{4}{14}$ (KO,NO_5), $1\frac{4}{14}$ (HO,SO_3) and $\frac{10}{14}$ (HO,NO_5); and if 3 equivalents of sulphuric acid be employed to 1 of nitrate of potash, since the mass a of sulphuric acid is now $= 3$; $ax : \beta y$ as

15 : 4; consequently the proportions of the ingredients would be $1\frac{5}{9}$ (KO,SO_3), $\frac{4}{19}$ (KO,NO_5), $2\frac{4}{19}$ (HO,SO_3), and $1\frac{5}{9}$ (HO,NO_5); the proportion of sulphate of potash continuing to increase, though in a decreasing ratio, for every addition of free sulphuric acid to the solution.

(857) *Gladstone's Experiments on Mass.*—No experimental solution of this problem was given by Berthollet, and the question fell into abeyance; but within the last few years several attempts have been made with considerable success to determine this question quantitatively. Gladstone (*Phil. Trans.*, 1855, p. 179) has published a series of experiments in which he has made use of the change of colour which solutions of certain salts undergo on mixture with each other, as a means of ascertaining the extent to which this mutual decomposition proceeds when all the products remain in solution. The principle of his experiments will be easily understood. Solutions of several persalts of iron, such as the persulphate, the pernitrate, perchloride, peracetate, percitrate, &c., were prepared in such a manner that each should contain the same proportion of the sesquioxide dissolved in the same bulk of water (each of the solutions employed contained very nearly 1 grain of sesquioxide of iron in 1000 grain-measures of water). A solution of pure sulphocyanide of potassium was then prepared of such a strength, that when 1 measure of this solution and 4 of that of the iron salts were mingled, the proportion of sulphocyanogen should be exactly sufficient to convert the whole of the iron into persulphocyanide, if complete mutual decomposition occurred: thus the proportions of the two salts employed were such that it would be possible for exact mutual interchange to occur as represented in the following equation: $Fe_2O_3, 3\,NO_5 + 3\,(K,Scy) = Fe_2\,Scy_3 + 3\,(KO,NO_5)$. On making the experiment in this manner, it was found that the iron was never wholly converted into the red salt, for the tint was deepened by the addition of more either of the iron salt or of the sulphocyanide. In order to obtain a quantitative estimate of the amount of these effects, definite measures of the solutions of pernitrate of iron and of sulphocyanide of potassium were mixed together, and the liquid so obtained was diluted with water until it occupied a known, but arbitrary volume. This diluted mixture furnished a liquid of a certain depth of colour which was employed as a standard of comparison. Another measure of the solution of pernitrate of iron, equal to that used in the standard solution, was mixed with regulated additions of the sulphocyanide of potassium, and the liquid thus obtained was diluted with measured quantities of water after each addition of sulphocya-

nide, until, as far as the eye could distinguish, this solution had the same depth of tint as that employed as the standard; it was then assumed that the quantity of sulphocyanide of iron formed was proportionate to the bulk of the two solutions.* Suppose that the standard solution occupied a volume of 880 measures. It was found that if twice the quantity of the sulphocyanide of potassium employed in the standard liquid were made use of in the new solution, this mixture would require dilution till it occupied 1270 measures. The proportion of sulphocyanide of iron formed in these two cases, was assumed to be as 880 to 1270, or as 1 to 1·44. The excess of sulphocyanide thus employed had therefore withdrawn an additional quantity of iron from its combination with the nitric acid.

In this manner experiments were made with quantities of the sulphocyanide of potassium, progressively increasing from $\frac{1}{4}$ equivalent of the sulphocyanide to each equivalent of nitrate of iron, up to 375 equivalents of sulphocyanide to 1 equivalent of nitrate of iron, and it was found that the quantity of sulphocyanide of iron which was formed, continued to increase with every addition of sulphocyanide of potassium, though the effect of each consecutive addition became less and less marked.

It was ascertained, as indeed it was to be expected, that the proportions of sulphocyanide of iron, which are formed by the mixture of equivalent quantities of other salts of iron with given amounts of the sulphocyanide of potassium, vary with the nature of the acid in combination with the peroxide of iron. For example, it was found that when nitrate of iron was mixed with sulphocyanide of potassium, in the proportion of equivalent quantities of each, that 0·194 of an equivalent of the red salt was formed. When an equivalent of sesquichloride of iron was used, 0·173 of an equivalent was formed; when the sulphate was employed, 0·126 of an equivalent was produced; with acetate of iron 0·04 only was formed, and when citrate of iron was employed, the quantity of sulphocyanide of iron which it yielded was too small to admit of being estimated. The oxide of iron therefore retained these different acids with degrees of force which vary inversely with the quantity of sulphocyanide which is formed, whilst the potassium in the sulphocyanide attracted them with a power in direct proportion to these quantities. Various attempts have been made to obtain

* Gladstone found that simple dilution of the sulphocyanide of iron reduced the tint in a proportion greater than could be accounted for by mere dilution; but this source of error was eliminated, and was not found to present itself in other cases which he employed to test the accuracy of the general conclusion.

relative numerical expression for the force of affinity by which different compounds are united, but they have all hitherto failed. Experiments conducted upon the principle of those of Gladstone appear to offer the fairest prospect of solving this interesting and important problem.

Besides the sulphocyanide of iron, Gladstone examined a variety of other coloured compounds; one of which was the scarlet bromide of gold, which becomes yellow when mixed with the chlorides of potassium and sodium, to an extent varying with the proportion in which these salts are added: the sulphate of quinia, when mixed with a soluble chloride, iodide, or bromide, also afforded similar indications, as it loses its *fluorescent* character (104) in proportion to the quantity of chloride or bromide with which it is mixed. From these and from a variety of other experiments, it appears that when two or more compounds in solution are made to act upon each other, provided that the products which they form by their mutual action are also soluble, the following conclusions may be drawn:—1. That mutual interchange between the bodies which are mixed takes place in determinate proportions. 2. That these proportions are independent of the manner in which the compounds were originally combined: thus, if sulphate of potash and pernitrate of iron be mixed in equivalent quantities, the result is the same as if nitrate of potash and persulphate of iron had been employed in equivalent quantities. This is a fundamental point in these inquiries; but if Struve's observations (quoted by Graham, *Elem. Chem.* 2nd Ed. p. 232) be correct,—viz., that in the preparation of mineral waters, the taste of the liquid varies, not only according to the nature of the salts, but also according to the order in which they are added,—it cannot be a general law. 3. That these proportions are dependent partly upon the strength of the mutual affinities of the components for each other, and partly also upon the *mass*, or relative proportion of each compound which is present in the mixture. 4. That the alteration of the mass of any one of these compounds alters the amount of all the other compounds which co-exist in the mixture, in a regularly progressive ratio; and these quantities admit of being represented by regular curves. In most cases this adjustment of the relative quantities of the different bodies takes place immediately that the mixture is made.

(858) *Experiments of Bunsen and of Debus.*—The results are different if the products of the chemical combination be at once removed from the sphere of action,—as by the formation of gaseous compounds, or of an insoluble precipitate when two liquids are mixed. Bunsen has investigated the results obtained in some

cases of gaseous combination. He found that when a mixture of hydrogen and carbonic oxide was detonated with oxygen in quantity insufficient for its complete combustion, the oxygen divided itself between the two gases in such a manner that the quantities of water and of carbonic acid produced were in very simple atomic relations to each other (*Liebig's Annal.*, lxxxv. 137). He exploded together mixtures of oxygen, hydrogen, and carbonic oxide, in varying proportions, the hydrogen and carbonic oxide being each in considerable excess over the oxygen: under such circumstances water and carbonic acid were formed; but the quantity of carbonic acid was greater, in proportion as the carbonic oxide preponderated, according to a certain law. Similar results were obtained by detonating cyanogen with a quantity of oxygen insufficient for its complete combustion; in such case nitrogen and a mixture of carbonic acid and carbonic oxide in simple proportions were obtained: and when a mixture of carbonic acid and hydrogen was detonated with a quantity of oxygen insufficient for the consumption of the hydrogen, a certain proportion of the carbonic acid was reduced to carbonic oxide, according to the terms of the same law.

The following is the law deducible from Bunsen's experiments:—1. When two gaseous bodies, A, B, are mixed with a third body, C, and fired by means of the electric spark, the body C takes from A and B quantities which always stand to one another in a simple atomic relation: so that for 1 atom of A C, 1, 2, 3, or 4 atoms of B C are produced; for 2 atoms of A C, 3, or 5, or 7 atoms of B C are formed. If 1 atom of the compound A C, and one of B C be formed in this manner, the mass of A may be increased in the presence of B, up to a certain point, without any change in that atomic proportion; but if a certain limit be passed, the relation of atoms, instead of being as 1 : 1, suddenly becomes as 1 : 2, or as 2 : 3; and so on.

2. When a body, A, acting upon an excess of any compound, B C, reduces it, so that A C is formed, and B is set at liberty; then—if B in its turn can reduce the newly-formed compound, A C,—the final result is, that the reduced part of A C is in simple atomic proportion to the unreduced part. In the case of these reductions also, the mass of one of the ingredients of the mixture may be increased up to a certain point without altering the relative proportions of the compounds obtained; but if increased beyond this limit, a sudden alteration in the relative proportions of the products occurs; but these proportions still admit of being represented by simple ratios. This second portion of the law needs confirmation by more extended experiments.

The following experiments illustrate the first part of the fore-

going law:—On exploding mixtures of carbonic oxide and hydrogen, in the following proportions, Bunsen found that the quantities of carbonic oxide and hydrogen which were oxidized were in the proportions stated below:—

	Mixture detonated.			Ratio of Gases burned.	
	Oxygen.	Hydrogen.	Carb. Oxide.	Hydrogen.	Carb. Oxide.
I.	10	20	79·4	1	2
II.	10	20	44·4	2	2
III.	10	20	12·1	6	2
IV.	10	37	31·5	8	2

These experiments show that, as the proportion of carbonic oxide to the hydrogen in the mixture decreased, the proportion oxidized on detonation decreased also, but it decreased *per saltum*, not gradually, and these proportions were found to be uniformly the same on repeating the detonation with the same mixture, although the degree of compression to which the mixture was subjected during the detonation was considerably varied in different experiments.

The following are Bunsen's principal experiments in support of the second part of the foregoing law:—When carbonic acid is driven over ignited charcoal, it is wholly converted into carbonic oxide; but when steam is transmitted over ignited charcoal, a mixture of hydrogen, carbonic oxide, and carbonic acid is produced, in the proportion of 4 volumes of hydrogen, 2 of carbonic oxide, and 1 volume of carbonic acid. Again, when a mixture of cyanogen with atmospheric air and oxygen was detonated in the eudiometer in the proportion of 6·2 of cyanogen to 10 of oxygen;* the cyanogen yielded 3 volumes of nitrogen, 2 of carbonic oxide, and 4 of carbonic acid: and when a mixture of 4·07 of carbonic acid, 33·25 of hydrogen, and 10 of oxygen was detonated, a portion of the carbonic acid yielded oxygen to the hydrogen, and was reduced to the state of carbonic oxide; 3 volumes of carbonic oxide being formed, whilst exactly 2 volumes of carbonic acid remained unacted upon, although a large excess of hydrogen was present.

Debus arrived at substantially the same results as those indicated by Bunsen for gaseous mixtures, by precipitating a mixture of lime and baryta water, by small proportions of a solution of carbonic acid, and by similar experiments upon a large excess of a dilute solution of the mixed chlorides of calcium and of barium to which a dilute solution of carbonate of soda was added.

In the experiments of Bunsen, it must be recollected that the

* Cyanogen requires for the complete combustion of its carbon twice its volume of oxygen, so that 6·2 of cyanogen would have required 12·4 instead of 10 of oxygen; there is therefore more oxygen than would suffice for the conversion of the carbon into carbonic oxide.

first products of the chemical combination are immediately removed from the sphere of action: carbonic acid, and carbonic oxide, and water will not mutually react upon each other; and in the experiments of Debus, the carbonates of the earths are insoluble—they are therefore at once withdrawn from further action upon the mixture.

(859) *Adhesion.*—The influence of adhesion in aiding chemical action is often exerted by overcoming the opposite force of elasticity: this is exemplified by the manner in which water frequently favours the mutual action of dry gases upon each other. For example, sulphurous acid and sulphuretted hydrogen may be mixed when dry without acting upon each other, but if water be present, the mutual decomposition of the two gases is the result. In like manner, when dry sulphurous acid and dry peroxide of nitrogen are mixed together, no combination takes place between them; the addition of a few drops of water, however, causes them immediately to condense and to form the white crystalline compound which has been spoken of when treating of the manufacture of sulphuric acid (344, and *note* p. 165). If the elasticity of these gases be overcome by other means—if, for instance, they be liquefied by exposing them to a low temperature—combination occurs without the intervention of moisture.

Water, by overcoming the self-repulsion of the gases, favours their chemical action upon solid bodies. Hydrochloric acid, and ammonia, in their gaseous form, generally exert but little influence upon the metals or upon their salts, although when in solution their action upon them is rapid and powerful.

Surface Actions.—The adhesion of gases to solids produces many curious phenomena:—for example, let a piece of charcoal be thoroughly saturated with hydrogen by attaching it to the negative wire of the voltaic battery, and employing it as the platinode in the decomposition of acidulated water: this charcoal, if now detached from the battery and thrown into a solution of sulphate of copper, or of nitrate of silver, will effect the decomposition of these salts, and their respective metals will be thrown down upon the charcoal in the reduced state; the charcoal and condensed hydrogen appearing to act the part of a voltaic circuit, in which the hydrogen supplies the place of the electro-positive or oxidizable metal, and the charcoal that of the electro-negative metal or conducting plate. If a plate of platinum, rendered chemically clean,* be

* This may be effected by holding the plate over the flame of a spirit-lamp and rubbing it, when hot, with a stick of caustic potash; the potash is to be maintained in a fused state upon its surface for a second or two; the alkali is then to be washed off completely in distilled water, and the plate is to be

introduced into a mixture of pure oxygen and hydrogen, in the proportions to form water, the gases become condensed upon the surface of the plate, and being brought within the sphere of each other's attraction, begin to unite; at first slowly, but during the act of combination, heat is extricated, and the action proceeds more quickly, until at last the plate becomes red hot, and an explosion of the gas ensues (Faraday, *Phil. Trans.*, 1834, p. 55). By employing the metal in a disintegrated or spongy form, the surface exposed is greater, and the action much more rapid: the metal conducts away but little of the heat which is generated, and soon bcomes red hot; whilst in the condition of platinum black (823) this activity attains its maximum. On throwing a little of this black powder into a mixture of oxygen and hydrogen it immediately becomes incandescent, and the gases combine with a loud report. Platinum may be obtained in a convenient state of fine subdivision for experiments of this nature, by moistening asbestos with a solution of bichloride of platinum and exposing it to a red heat; the chlorine is expelled, and a film of minutely divided platinum is left upon the surface of each fibre of asbestos.

From its inalterability by ordinary chemical agents, platinum in this finely divided form has been used to effect various combinations which cannot otherwise readily be procured between vaporized and gaseous bodies:—For instance, if ammonia be mixed with atmospheric air, and transmitted over spongy platinum gently heated, its nitrogen becomes converted into nitric acid, and its hydrogen into water; $H_3N + 8\ O = 3\ HO,NO_5$: but this transformation cannot be effected by heat, unless some substance analogous to spongy platinum be used, since nitric acid is decomposed at a temperature which, under ordinary circumstances, is required to effect the combustion of ammonia. On the other hand, ammonia may be formed from the oxides of nitrogen, by mixing them with hydrogen and transmitting the gases over platinum sponge gently heated; $NO_2 + 5\ H = H_3N + 2\ HO$. Nitrate of ammonia, when heated with platinum black, yields nitric acid, nitrogen, and water, instead of protoxide of nitrogen; thus $5\ (H_4NO,NO_5) = 2\ NO_5 + 8\ N + 20\ HO$. A variety of other interesting changes may be effected. According to Döbereiner, (who first pointed out the remarkable power which finely divided platinum possesses of effecting combinations of this kind,) a mixture of cyanogen and hydrogen by the aid of a gentle heat is partially

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immersed for a minute in hot oil of vitriol; after which it is to be freed from adhering acid by immersion for a quarter of an hour in a large bulk of distilled water.

converted into cyanide of ammonium when in contact with spongy platinum. In a mixture of binoxide of nitrogen and olefiant gas, carbonate of ammonia is produced; and in a mixture of the vapour of alcohol and binoxide of nitrogen, cyanide of ammonium, carbonate of ammonia, olefiant gas, water, and a deposit of carbon are formed. In like manner, sulphurous acid may be rapidly converted into sulphuric acid, if it be driven, in a moist state, mingled with air, through tubes containing spongy platinum: this method was even proposed as a manufacturing process for obtaining oil of vitriol, but it was abandoned in consequence of a gradual alteration in the platinum, by which it is deprived of this power of effecting combination. Platinum black produces with the vapours of alcohol in contact with atmospheric air, a series of compounds which are finally converted into acetic acid (62):—

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} + 4\,O = \overbrace{C_4H_4O_4}^{\text{Acetic Acid.}} + 2\,HO.$$

For the success of these experiments, it is necessary that the surface of the platinum be chemically clean, otherwise the supposed adhesion of the gases or vapours to the metal does not take place. Faraday considers that these actions are owing to the adhesion of the gases to the surface of the metal, by which the particles of one gas are brought into chemical contact with those of the other. He observed that the admixture of small quantities of carbonic oxide, or of the vapour of bisulphide of carbon, or of olefiant gas,* prevented the platinum from effecting the combination of the oxygen and hydrogen, but did not deprive the metal of its activity, as was ascertained by afterwards plunging it into a mixture of pure oxygen and hydrogen. On the other hand, the addition of sulphuretted or of phosphuretted hydrogen to an explosive mixture of oxygen and hydrogen, not only prevented the combination from being produced by the platinum, but it effected such an alteration of the surface of this metal that when it was plunged into a fresh portion of mixed oxygen and hydrogen, no combination of the gases occurred. Hydrochloric acid also rapidly destroys the peculiar properties of finely divided platinum. According to Döbereiner, the preventive action of this gas depends upon the decomposition of the hydrochloric acid by the oxygen condensed upon the platinum:

* Graham finds that in the case of carbonic oxide, a gradual oxidation of the carbonic oxide takes place, but that this action is much slower than the oxidation of the hydrogen; the oxidizing influence is wholly concentrated on the carbonic oxide, and until this gas is entirely oxidated the hydrogen remains unaltered in the mixture.

water is formed, whilst chlorine is liberated, and this chlorine, by converting the platinum superficially into protochloride, destroys its power; its activity, however, can be restored by treating it with boiling oil of vitriol. Hydrochloric acid is in this case expelled, and a small quantity of protoxide of platinum is dissolved; the metal is then to be well washed in distilled water.

(860) Other finely divided substances besides platinum possess this property of favouring the combination of oxygen and hydrogen in an inferior degree; even pounded glass, porcelain, charcoal, pumice, and rock crystal, if warmed to 600°, produce this effect. Finely divided palladium, rhodium, and iridium also determine the combination of oxygen and hydrogen with explosion at ordinary temperatures. Gold and silver effect the combination of hydrogen with oxygen quietly, at temperatures far below the boiling point of mercury (Dulong and Thénard). Metals which have a strong affinity for oxygen cannot be used, because they immediately become oxidized upon their surface.

(861) *Catalysis.*—The remarkable actions produced by the agency of finely divided platinum have in the foregoing paragraphs been attributed to the force of adhesion, which is supposed to bring the different gaseous bodies within the sphere of mutual action; but they were viewed by Berzelius as arising from a new force, which he termed *catalysis*, in virtue of which, he says:—'Certain bodies exert, by their contact with others, such an influence upon these bodies, that chemical action is excited; compounds are destroyed, or new ones are formed, although the substance by which these actions are induced does not take the slightest part in these changes.' This catalytic force, however, is probably purely imaginary; most of the phenomena which have hitherto been referred to its agency being occasioned by several different causes, which often admit of being distinguished from each other, and which may, as in the case of the action of platinum, be explained by the active operation of other known forces.

One class of these phenomena is that included under the term *fermentation.* Fermentations are peculiar to the products of organic chemistry; such for instance, as the change of solution of sugar into alcohol and carbonic acid, under the influence of *yeast:* the change of starch into sugar in the operation of mashing wort, or the germination of seeds, owing to the presence of a peculiar albuminous substance termed *diastase:* and the gradual conversion of amygdalin, the bitter principle in the bitter almond, into hydrocyanic acid, oil of bitter almonds, sugar and formic acid, when it is dissolved in water, and mixed with *synaptase,* or the albuminous

principle contained in the pulp of the seed. In all these cases, however, although the constituents of the yeast, the diastase, or the synaptase, do not enter into the formation of the new products, yet they disappear during the change, and during the whole time are undergoing a series of specific alterations, which stand in intimate but unexplained relation to the metamorphosis of the sugar, the starch, or the amygdalin. One of the most remarkable features of these decompositions, is the small proportion of the ferment, or *catalytic body* as Berzelius termed it, which is required to produce the change: for instance, 1 part of yeast, calculated in its dry state, is sufficient to convert 60 parts of sugar into alcohol and carbonic acid; and a still smaller quantity is required in the case of diastase, 1 part of which is able to effect the transformation of more than 1000 times its weight of starch into sugar. The consideration of these remarkable metamorphoses must however be deferred until the organic bodies themselves have been described.

Liebig's theory of catalysis is, 'that a body in the act of combination or decomposition, enables another body, with which it is in contact, to enter into the same state. It is evident,' says he, 'that the active state of the atoms of one body has an influence upon the atoms of a body in contact with it, and if these atoms be capable of the same change as the former, they likewise undergo that change, and combinations and decompositions are the consequence. * * * This influence exerted by one compound upon the other, is exactly similar to that which a body in the act of combustion exercises upon a combustible body in its vicinity; with this difference only, that the causes which determine the participation and duration of these conditions are different.'

These explanations are hardly sufficient to account for the phenomena of fermentation, as the bodies which are undergoing fermentation do not 'enter into the *same* state' as the particles of the ferment; but they apply admirably to many of the illustrations cited by Liebig in proof of his theory. Amongst these illustrations is an experiment by Saussure, who observed that moist woody fibre, if placed in contact with oxygen, gradually converts the oxygen into carbonic acid. On adding a certain quantity of hydrogen to a measured bulk of oxygen, which was undergoing this change, he observed a diminution in the volume of the two gases immediately after making the mixture; a portion of oxygen had thus been caused to enter into combination with the hydrogen, and a true gradual combustion of the hydrogen had been effected, analogous to that produced by platinum, owing to

its contact with vegetable matter which was itself undergoing slow oxidation.

Again, it has been observed in the case of certain alloys, that the compound is entirely soluble in an acid which may be unable to attack one of the components of the alloy when in a separate form. Platinum, for instance, is not soluble in nitric acid, but if it be alloyed with 10 or 12 parts of silver, the acid dissolves it readily. In like manner, copper is insoluble in diluted sulphuric acid; but an alloy of zinc, nickel, and copper is readily dissolved by this liquid.

(862) *Effects of Motion on Chemical Affinity.*—In many cases motion favours the manifestation of cohesion in a remarkable manner: for example, water may be cooled below its freezing point, and may retain its liquid form if it be kept perfectly motionless, but on the slightest agitation it assumes the form of ice. Again, if a solution of nitrate of silver be simply mixed with hydrochloric acid, it will long remain milky; but if the nitrate be in excess, and the mixture be briskly shaken for about a minute, the whole of the chloride of silver will collect into dense flocculi, which subside rapidly and leave the liquid clear. In a somewhat similar manner motion favours the development of chemical action:—thus a mixture of tartaric acid and nitrate of potash may be made, and no sign of precipitation will appear for many minutes, if the mixture after simple agitation be left at rest: but if it be briskly stirred with a glass rod, an abundant deposition of crystals will speedily be produced. A similar effect is often observed with other crystalline precipitates: the double chloride of platinum and potassium, or of platinum and ammonium, frequently does not appear in dilute solutions until the mixture has been briskly stirred. If the glass rod which is used in stirring the mixture be drawn against the side of the vessel containing the liquid, the track of the rod will be rendered evident by the formation of crystals, which are symmetrically deposited on each side of this line. This effect is particularly manifested when a solution of phosphate of soda is added to dilute neutral solutions of magnesia containing ammoniacal salts; the double phosphate of ammonia and magnesia takes many hours for its complete deposition, unless the liquid be briskly stirred.

Sometimes when the chemical affinities which hold a compound together are feeble, or where the components have a strong tendency to assume the gaseous form, a blow will be sufficient to disturb the equilibrium, and an explosion will follow. In this way chloride of nitrogen, which is united by feeble affinities, and is composed of bodies which naturally exist in the gaseous state, is sometimes decomposed by the mere fall of a drop of the liquid

to the bottom of a jar of the solution in which it is being formed. The ordinary percussion-cap is another instance of the same kind, where the nitrogen in the fulminic acid suddenly resumes its gaseous state on the application of a blow. In the latter case, and in that of the common lucifer match, it might be supposed that the heat devolved by the sudden compression attending the blow or the friction, is the cause of these detonations; but this explanation certainly cannot apply to the iodide of nitrogen, which, if dry, explodes when touched even with a feather. Fulminating silver is also decomposed with explosion by causes equally slight.

(863) *Concurring Affinities.*—Another class of these so-called catalytic phenomena is exemplified in the effect of the admixture of oxide of copper, or oxide of manganese, in aiding the decomposition of chlorate of potash. Chlorate of potash fuses at about 650°, and when heated to about 700° it is decomposed with effervescence and rapid evolution of oxygen: when mixed with about a fourth of its weight of black oxide of copper, or of oxide of manganese, the salt begins to be decomposed at a temperature of between 450° and 500° (much below its fusing point); the gas which is given off in this case, however, is always accompanied by a small quantity of chlorine. Other oxides produce a similar effect, but the temperature required varies with each oxide: thus, I find when the chlorate is mixed with sesquioxide of iron it requires a temperature of about 500°; with oxide of lead a somewhat higher temperature is needed; whilst magnesia and oxide of zinc do not aid the decomposition of the salt at all.

This remarkable decomposition appears to admit of an explanation, suggested by Mercer, in elucidation of other somewhat analogous actions. He supposes, although the catalytic body is not found to have experienced any perceptible alteration after the decomposition is complete, that it acts by exerting a feeble chemical affinity upon one of the constituents of the compound. In the case of oxide of manganese and chlorate of potash, the oxide of manganese is a substance which has an affinity for an additional quantity of oxygen, as is evinced by the possibility of forming manganic and permanganic acids from it by further oxidation. This tendency, although it does not rise high enough in the experiment before us to produce the acids, may yet exert sufficient attraction upon the oxygen to facilitate its escape. Indeed it is not impossible that traces of manganic acid may be actually formed, and then decomposed; in which case the formation of the small quantity of potash, and the liberation of the chlorine, which always accompanies the oxygen, would be accounted

for. A somewhat similar explanation may be applied in the case of the black oxide of copper; an unstable sesquioxide of this metal appears to exist: black oxide of copper therefore has a feeble affinity for oxygen, and though that affinity is not adequate to retain the oxygen when separated from the chlorate of potash, it may yet aid in effecting its liberation: sesquioxide of iron is also susceptible in the ferric acid of a higher but unstable stage of oxidation, and the same holds good of oxide of lead; hence these compounds facilitate the decomposition of the chlorate. There is no proof of the existence of a higher oxide either of magnesium, or of zinc, and accordingly we find that scarcely any effect is produced on heating these oxides with the chlorate. I find also that powdered glass and pure silica are equally inert, probably from the same cause.

Mercer observed that starch, which is ordinarily converted by nitric acid into oxalic acid, is entirely transformed into carbonic acid if a salt of manganese be present; 4 CO_2 being formed, instead of 2 HO,C_4O_6. Oxalic acid, also, may be in this manner rapidly converted into carbonic acid (Playfair, On Catalysis, *Proceed. Chem. Soc.*, iii. 351). If an ounce of oxalic acid be dissolved in 10 ounces of water, at 180°, and 1 ounce of colourless nitric acid, sp. gr. 1·30, be added, no decomposition of the oxalic acid occurs; but it immediately commences on adding a small quantity of a solution of nitrate of manganese, or any other salt of this metal. The protoxide of manganese, from its tendency to pass into the state of peroxide, tends to deprive the free nitric acid of oxygen, and aids the oxalic acid to decompose this acid; and the oxalic acid having a stronger affinity for oxygen than the protoxide of manganese, immediately appropriates the oxygen; the united affinities of both being able to accomplish a decomposition which could not have been effected by either separately. An analogous instance of the effect produced by concurring affinities of a more energetic kind is seen in the power possessed by chlorine to decompose silica or alumina when these oxides are mixed with charcoal (388, 566), though neither chlorine nor charcoal is able separately to produce this effect upon them.

A similar result is obtained when a quantity of hydrated oxide of copper, or of peroxide of manganese, is thrown into a mixture of bleaching powder and water; on warming the mixture, oxygen is evolved abundantly, and chloride of calcium is formed; the oxide of copper or of manganese, by its affinity for oxygen, aids the elastic force developed by heat in detaching the oxygen from the chloride of lime, and the oxygen, by its elasticity,

escapes in the gaseous form without combining with the metallic oxide.

Gaseous ammonia may be passed through heated porcelain tubes at a very high temperature, and it will experience only a partial decomposition ; but if the tube be filled with finely divided metallic copper or iron, the decomposition takes place with facility at a lower temperature. It is not improbable that in this case the metals act by their affinity for nitrogen, which is feeble, and that a nitride of copper or of iron may be formed (448). If iron wire be employed instead of finely divided iron, it is found to have become superficially altered and brittle. Platinum favours the decomposition of ammonia but slightly, and glass scarcely in any appreciable degree.

Alcohol, when exposed to the air, evaporates without undergoing any chemical change, but if a quantity of caustic potash be dissolved in the alcohol, the alkali appears to enhance its affinity for oxygen; in consequence of which acetic and formic acids are produced, and combine with the potash.

The decomposition of binoxide of hydrogen (396) by contact with many bodies, which appear to undergo no chemical alteration during the action, may possibly be referred to the same cause. When, for example, finely divided metallic gold, silver, or platinum, or peroxide of manganese, is placed in the liquid binoxide, the latter is decomposed, the oxygen being attracted by the metal, which, however, has not sufficient power to retain it in combination. A singular circumstance, however, has been observed, when oxide of gold or oxide of silver is substituted for the metals themselves; decomposition of the binoxide is produced by the metallic oxide, but the oxide of gold or of silver at the same time parts with its oxygen, and is reduced to the metallic state. A similar reaction happens if an acid solution of bichromate of potash be mixed with the binoxide of hydrogen, the chromic acid losing half its oxygen simultaneously with the binoxide of hydrogen.*

* Brodie (*Phil. Trans.* 1850, p. 759) has published the results of a series of experiments, showing that in such decompositions there is a numerical relation between the quantity of the binoxide which is decomposed and of the metallic oxide which is reduced. These experiments, however, were chiefly made upon binoxide of barium, as being much more manageable than binoxide of hydrogen. It was found that when the binoxide was mixed with water, and placed in contact with oxide, or with chloride of silver, that both the compound of barium and that of silver was decomposed; baryta, or chloride of barium, being formed, whilst metallic silver and oxygen gas were liberated. A nearly uniform quantity of peroxide of barium was employed in each experiment, whilst the quantity of oxide, or of chloride of silver, was progressively increased: it was found that the silver compound was never wholly reduced, but that the proportion of it which underwent decomposition bore an increasing

Other substances besides binoxide of hydrogen exhibit a similar susceptibility to decomposition by contact with certain bodies. Persulphide of hydrogen, for example, is immediately decomposed by contact with oxides of manganese and silver, and like the binoxide of hydrogen, it is rendered more stable by the addition of acids, while its decomposition is facilitated by contact with alkalies. The nitrosulphates (354) discovered by Pelouze, afford another instance of decomposition effected by a body which undergoes no *apparent* change; but this decomposition is particularly instructive, as it is almost certain that the body which excites the decomposition does suffer a *real* chemical change. Thus the addition of a solution of sulphate of copper to a solution of nitrosulphate of ammonia causes an immediate effervescence, owing to the escape of protoxide of nitrogen. This decomposition appears to be produced thus:—on the addition of sulphate of copper, the nitrosulphate partially exchanges bases with it; now so long as the nitrosulphuric acid is in combination with an alkali, the acid has a certain stability, since the alkalies appear by their basic energy to preserve the elements of the acid in equilibrio; but as soon as a salt with a weaker base is added, such as the sulphate of copper, a portion of nitrosulphate of copper is formed; but the oxide of copper being no longer able to maintain this balance, the elements of the acid arrange themselves in a new order: for instance—

$$\overbrace{H_4NO,SO_2NO_2}^{\text{Nitrosulph. Ammon.}} + \overbrace{CuO,SO_3}^{\text{Sulph. Copper.}} = \overbrace{H_4NO,SO_3}^{\text{Sulph. Ammon.}}, + \overbrace{CuO,SO_2NO_2}^{\text{Nitrosulph. Copper.}};$$

and the nitrosulphate of copper immediately breaks up into protoxide of nitrogen and sulphate of copper; CuO,SO_2NO_2 becoming $CuO,SO_3 + NO$. Consequently sulphate of copper is found in the liquid at the close of the reaction *apparently* unaltered.

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ratio to the amount of peroxide of barium which was decomposed, as the quantity of oxide or of chloride of silver was increased. In no case, however, was the amount of oxide or of chloride of silver reduced quite equivalent to the proportion of oxygen eliminated from the peroxide of barium. Brodie connects these experiments with an ingenious speculation, by which he endeavours to account for the simultaneous liberation of oxygen from the peroxide of hydrogen or of barium and from the oxide of silver, and which he applies to chemical decompositions generally: he supposes that the *particles of the same element* may, in certain circumstances, have an affinity for each other:—that for example, one equivalent of the oxygen of the peroxide of barium may be positive in its relation to the oxygen of the oxide of silver, which he supposes may be negative. In such a case the two particles of oxygen would mutually attract each other, and decomposition of both the oxides would be the result.

§ II. Influence of Heat upon Chemical Affinity.

(864) The forces which have as yet been considered do not manifest any specific effect in altering the amount of chemical affinity between any two bodies; but it is quite otherwise in the case of heat, which exerts a direct influence upon the degree of affinity. Elevation of temperature generally acts at once in augmenting the tendency to combination between the bodies which are submitted to its influence:—for example, sulphur or charcoal may be preserved at ordinary temperatures, in air or in oxygen, without change, for an indefinite period; but if sulphur be heated to 500°, and charcoal to a point a little below a red heat, oxidation commences, and proceeds with increasing vigour, and the phenomena of combustion occur. But although a rise of temperature exalts the action of chemical affinity, this tendency to combination is, at the same time, more or less counteracted, and is sometimes completely overcome, by the tendency to mutual repulsion which heat imparts to the molecules of all substances, both simple and compound. It not unfrequently happens that a moderate elevation of temperature produces combination, whilst a higher temperature destroys the compound so formed. A good instance of this kind occurs in the action of oxygen upon mercury: at ordinary temperatures this metal shows no disposition to combine with oxygen, for it evaporates in air and becomes condensed again in the metallic form; but at a temperature approaching 700°, or a little above the boiling point of the metal, it combines gradually with oxygen and becomes converted into the red oxide; whilst at a heat short of redness it is decomposed into gaseous oxygen and vapour of mercury. Again—baryta at a red heat absorbs a second equivalent of oxygen, forming peroxide of barium, but the second equivalent of oxygen is expelled by a full white heat, and the compound is reconverted into baryta. A mixture of oxygen and hydrogen may be preserved unchanged at ordinary temperatures, but the introduction of a glass rod heated to bare redness so completely alters their mutual affinity, that sudden combination attended with explosion is the result. This appears to be as pure a case of alteration of affinities as can be met with, since both the components are thoroughly mixed, and as both are in the gaseous state, heat cannot in this case act by diminishing cohesion, and so bringing their particles into more intimate contact. Grove, however, has shown that in the case of this same compound of oxygen and hydrogen a sudden inversion of affinity takes place,

for at an intense white heat they are separable from each other: by the voltaic ignition of a platinum wire under water, or by the intense heat of a ball of melted platinum raised to whiteness by an alcohol flame animated by a current of oxygen, and then plunged under water, the two gases may be separated from each other and collected in the gaseous state (*Phil. Trans.*, 1847).

Sometimes the decomposition effected by elevation of temperature is only partial; a new and more stable compound being formed, which, at a still higher temperature, is in its turn decomposed: thus olefiant gas at a full red heat loses half its carbon, and is converted into light carburetted hydrogen; and this gas, if subjected to a white heat, deposits the remainder of its carbon whilst pure hydrogen is liberated. Chlorate of potash at a moderate heat is decomposed into perchlorate, and probably into chlorite of potash: the latter salt, however, is immediately resolved into oxygen and chloride of potassium; but at a higher temperature the perchlorate in its turn parts with its oxygen, and the more stable chloride of potassium is the final result. Numerous other instances of this kind will be presented to the reader when the products of organic chemistry are examined.

A further illustration of this point is afforded by the different products which are furnished by the combustion of the same body at different temperatures. When a jet of cyanogen is burned with a free supply of air, the only products of the combustion are carbonic acid and nitrogen; but if a coil of red-hot platinum wire be suspended in a mixture of equal volumes of cyanogen and oxygen, the nitrogen undergoes oxidation as well as the carbon, deutoxide of nitrogen being formed, as is evidenced by the appearance of ruddy fumes, owing to the combination of the deutoxide with free oxygen. In a similar manner, ether, when burned freely in air, produces carbonic acid and water, $C_4H_5O + 12\,O$ becoming $4\,CO_2 + 5\,HO$; but if a glowing coil of platinum wire be suspended in a mixture of the vapour of ether and atmospheric air, several new products are formed, among which are aldehyd and acetic acid:—

$$\overbrace{(C_4H_5O)_2}^{\text{Ether.}} + 4\,O = 2\,\overbrace{(C_4H_4O_2)}^{\text{Aldehyd.}} + 2\,HO; \text{ and}$$

$$\overbrace{(C_4H_5O)_2}^{\text{Ether.}} + 8\,O = 2\,\overbrace{(C_4H_4O_4)}^{\text{Acetic Acid.}} + 2\,HO.$$

(865) *Suspension of Chemical Action by Depression of Temperature.*—As chemical affinity is increased, on the one hand, by elevation of temperature, so, on the other hand, it is diminished by

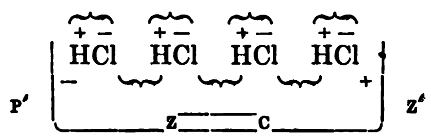
reduction of temperature. Schrötter has shown (*Chemie*, vol. i. p. 129) that, by a sufficient degree of cold, chemical combination may be prevented even between bodies which at the ordinary temperature of the air unite with each other with great energy. Chlorine, for example, combines with phosphorus, or with finely-divided metallic antimony or arsenic, with such violence that these bodies take fire spontaneously in an atmosphere of the gas; but if the chlorine be cooled down to —106°, by means of a bath of solid carbonic acid and ether (182), it remains liquid at the ordinary pressure of the air, and it is then quite indifferent to the phosphorus, the arsenic, or the antimony, provided these substances be cooled to the same temperature before they are added to the liquid chlorine. When the tube in which the mixture is contained is withdrawn from the cold bath, the evaporation of the chlorine occurs with sufficient rapidity to preserve the temperature below the point of combination; but if the free escape of the chlorine be prevented, the temperature rises, and combination occurs with explosive violence. The mutual action of chlorochromic acid and alcohol, of chlorine and ammonia, of iodine or of bromine and phosphorus, and various other actions of a similar nature, may be prevented in the same way.

From these experiments, and from those detailed in the foregoing paragraph, it appears to be not improbable that when two bodies have an affinity for each other, there is a certain range of temperature within which they will enter into combination, but if the temperature be raised or depressed beyond a certain limit, their mutual affinity is suspended; and at high temperatures the compound already formed may be destroyed. The temperature most favourable for combination varies with each pair of bodies, and it seems to be probable that there is for each a certain temperature at which the maximum of affinity exists, and above or below which it decreases.

§ III. Influence of Electricity on Chemical Affinity. Electrotyping, Voltaic Plating, &c.

(866) The suspension of chemical action which occurs under the influence of electrical induction is one of the most interesting circumstances which modern discoveries have brought to light. As an instance of this kind, we may cite the manner in which zinc, when placed in contact with copper beneath the surface of sea water, acts in preventing the corrosion of the copper, and

transfers to itself the chemical energy which would otherwise be manifested upon the copper (229). A similar suspension of chemical action is produced in the ordinary case of the decomposition of water between two platinum electrodes by the voltaic current: here the electricity appears to act by weakening, or rather by partly neutralizing, ordinary affinity in one direction, whilst it strengthens or adds to it in the opposite, and hence the particles which were previously in combination with each other lose their affinity one for the other, and acquire it for those particles which are next adjacent to them in the liquid; thus, if the brackets above the subjoined formulæ indicate the state of combination of the elements of hydrochloric acid before the passage of the current, the brackets below would indicate the effect produced after its transmission, thus:—



Here Z C is supposed to represent the battery, and P′ and Z′ the platinode and zincode of the arrangement: the positive electricity of the zincode seems to detach the chlorine adjacent to it from the hydrogen with which it was previously in combination, whilst the negative electricity of the platinode produces a similar effect upon the contiguous particles of hydrogen, and the intermediate portions are polarized in the manner above represented.

The following modification of this experiment also shows in a striking manner the remarkable influence of electric polarity upon chemical affinity:—If two separate glasses filled with diluted sulphuric acid be placed side by side, and into one glass the platinode of the battery is plunged, whilst the zincode dips into the other cell, no decomposition will ensue; but if a connexion be established between the two glasses by means of a slip of platinum foil, one end of which is made to dip into each, the current will be immediately transmitted: hydrogen will be evolved upon the platinode in one glass, and oxygen upon the zincode in the other glass; whilst, owing to the polar condition into which the connecting slip of platinum is thrown, hydrogen will be given off from one end of the slip, and oxygen will be evolved upon the other extremity of it, although the metal itself experiences no sensible change beyond a slight rise of temperature.

(867) *Electrolysis of Salts.*—It has already been stated (247) that when a binary compound, such as a fused chloride, or an iodide,

is submitted to electrolysis, the ions or components of the compound are separated at the respective electrodes in equivalent proportions: the metal appearing at the platinode, whilst the chlorine, or corresponding element, is deposited at the zincode. If the zincode of the battery be formed of a substance capable of combining with the chlorine or corresponding element, an equivalent amount of the chloride or other compound of this metal will be formed there; and when the metal of the zincode is the same as that contained in the compound which is undergoing decomposition, the original compound is reproduced. Thus, if a quantity of fused chloride of silver ($AgCl$) be decomposed by a current which is conducted into it by means of silver wires, the quantity of the chloride will undergo no alteration; for in this experiment, as fast as the silver is deposited upon the negative wire, a corresponding amount of silver will be dissolved from the positive wire, since the latter wire combines with the equivalent quantity of chlorine which is liberated at this point. Let Ag + represent the positive silver wire, or zincode, by which the current is conveyed into the melted chloride, and —Ag the negative wire: if the brackets in the upper row of symbols which follow indicate the combination before the passage of the current, the lower ones will show the arrangement after the occurrence of the decomposition:—

$$-\mathrm{Ag}\,|\,\underline{\overbrace{\mathrm{AgCl}}\ \overbrace{\mathrm{AgCl}}\ \overbrace{\mathrm{AgCl}}}\,|\,\mathrm{Ag}+$$

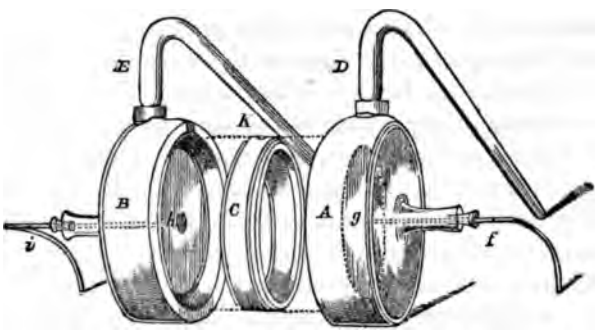
$$\mathrm{AgAg}\,|\,\underline{\overbrace{\mathrm{ClAg}}\ \overbrace{\mathrm{ClAg}}\ \overbrace{\mathrm{ClAg}}}\,|$$

An examination of the products furnished by the electrolytic decomposition of solutions of the oxysalts in water, exhibits results which appear to be at variance with the statement that the components of an electrolyte are separated in equivalent proportions, but further investigation shows that they are strictly in accordance with it; these experiments also lead to very interesting conclusions which have an important bearing upon the theory of salts in general.

When a solution of an oxysalt such as sulphate of soda is submitted to electrolysis, a quantity of acid accumulates around the positive plate, and of alkali around the negative plate; whilst at the same time both oxygen and hydrogen are set free. The proportions of each may be determined by means of a diaphragm apparatus, in which the products of decomposition can be kept separate from each other, and the gases which are evolved can be separately collected. Such an apparatus was contrived by Daniell,

and is represented in fig. 348. A and C are the two halves of a stout glass cylinder, which are fitted by grinding upon a hollow ring of glass, C; the two rims of this ring are ground down to a grooved shoulder, so as to allow a thin piece of bladder to be tied over each end of the ring, which thus constitutes a kind of drum; at K is a small hole through which the cavity thus formed can be filled with liquid; D and E are two bent glass tubes for carrying off the gases evolved during electrolysis; *g* and *h* are two large platinum electrodes, which pass through corks in the necks of the cylinder, and can be connected with the battery by means of the

FIG. 348.



wires, *f*, *i*. The apparatus thus forms three compartments, which may be filled with the liquid for experiment, and the whole may be supported in a frame of wood. By the employment of this apparatus, it is found that while a quantity of acid accumulates at the zincode, an equivalent amount of alkali is set free at the platinode. At the same time, a quantity of gas is also emitted from each electrode, that from the zincode being oxygen, and that from the platinode, hydrogen. Upon placing a voltameter in the course of the circuit, it is found that a quantity of gas is emitted from the saline liquid, exactly equal to that obtained from the voltameter; and upon neutralizing the acid and alkali, they likewise are in equivalent proportions to the gas which is emitted (Daniell, *Phil. Trans.*, 1839 and 1840).* Suppose that the gas collected in the voltameter amount to 71 cubic inches (or the quantity yielded by 9 grains of water at 60° F., Bar. = 30 inches), the united quantity

* This observation is *strictly* true, as I have found by numerous careful repetitions of these experiments, although, as Magnus (*Pogg. Annal.* cii. 1) has pointed out, when the quantity of acid and alkali becomes considerable in the two cells, the liberated acid and alkali each transmit a portion of the current as well as the sulphate of soda, so that if the experiment be unduly prolonged, the proportion of the acid and base set free is less than that which theory requires.

of oxygen and hydrogen from the solution of sulphate of soda would be the same,—and, in addition, one equivalent in grains, or 71 grains of sulphate of soda would be decomposed; 31 grains of soda would be liberated at the platinode, and 40 grains of sulphuric acid at the zincode. Upon substituting a voltameter of fused chloride of lead in the circuit for one containing diluted sulphuric acid, and still continuing to transmit the current through the solution of sulphate of soda, it was found that for every equivalent of chloride of lead which was decomposed, 1 equivalent of the mixed gases was evolved from the saline solution, and at the same time 1 equivalent of the sulphate was decomposed. What is observed in the case of sulphate of soda holds good also with the oxysalts of the alkalies and earths generally.

(868) *Bearing of Electrolysis on the Binary Theory of Salts.*— It is a fundamental law of voltaic action, that the amount of force circulating in any circuit at the same time, is equal in every vertical section of the circuit, and consequently its decomposing energy in each section must also be equal; yet in the case of the sulphate of soda, there appears to be in the saline solution twice the amount of decomposition that occurs in the adjacent voltameter, though both are transmitting the entire current from the battery. A satisfactory and complete explanation of this anomaly is, however, effected by the *binary theory* of salts (454) in the following manner:—

Upon the binary theory of salts, the component ions of sulphate of soda are not soda and sulphuric acid (NaO,SO_3) but sodium and sulphion (a compound of 4 equivalents of oxygen and 1 of sulphur), (Na,SO_4), the compound being *sulphionide of sodium;* and such it proves to be under the influence of electrolysis, sodium being liberated at the platinode, whilst sulphion appears at the zincode. Sodium, however, cannot exist in the presence of water; the metal immediately takes oxygen, and becomes converted into soda; $Na+HO$ yielding $NaO+H$: the alkali is dissolved in the liquid, whilst the hydrogen escapes as gas. Sulphion is equally unable to exist in the separate form; it combines with hydrogen, $HO+SO_4$ becoming $O+H,SO_4$, while oxygen escapes, and sulphuric acid is formed: and as both sodium and sulphion are liberated in equivalent proportions, the quantity of water decomposed is also equivalent to the quantity of salt electrolysed.

On the foregoing view, therefore, the evolution of oxygen and hydrogen during the decomposition of saline solutions is a secondary action. If a solution of a salt of a metal which, like copper or lead, does not decompose water at ordinary temperatures, be substituted

for one of sulphate of soda as the electrolyte, no hydrogen should be evolved, but the metal itself should appear upon the platinode; whilst if the other constituent of the salt be one which, like chlorine, is unable to take hydrogen from water at common temperatures, no oxygen should be emitted. Accordingly, upon making the experiment with a solution of chloride of copper or of chloride of lead, the salt is resolved into metallic copper or metallic lead, and chlorine gas, but no oxygen or hydrogen, is liberated. These observations will explain the reason that although water, when pure, is scarcely decomposed by the current from 100 cells or upwards, yet it appears instantly to become a good electrolyte on the addition of a few drops of acid, or of solution of a salt of an earth or an alkali; for upon the addition of the salt it is this body which is decomposed, and the water is then resolved into oxygen and hydrogen by a secondary action in the manner already explained. Sulphuric acid in solution is in like manner resolved into hydrogen and sulphion, H,SO_4. In neither case is the water directly electrolysed. This observation also explains a circumstance which much perplexed the earlier experimenters upon the chemical action of the voltaic pile. In all experiments in which water was decomposed, both acid and alkali were invariably found to be liberated at the electrodes, although distilled water was employed; and hence it was believed for some time that the voltaic current had some mysterious power of generating acid and alkaline matter. The true source of these compounds, however, was traced by Davy (*Phil. Trans.*, 1807), who showed that they proceeded from impurities contained either in the water employed, or in the vessels made use of, or in the atmosphere itself. Having proved that ordinary distilled water always contains traces of saline matter, he redistilled it at a temperature below the boiling point, in order to avoid all risk of carrying over salts by splashing: he found that when he used marble cups to contain the water for decomposition, the acid was the hydrochloric and the alkali was soda, both derived from chloride of sodium present in the marble itself; when agate cups were used to contain the water he obtained silica; and when he used gold vessels, he procured nitric acid and ammonia, which he traced to atmospheric air; by operating *in vacuo* the quantity of acid and alkali was reduced to a minimum, but the decomposition then was almost arrested, although he operated with a battery of 50 pairs of 4-inch plates. Hence it is manifest that water itself is not an electrolyte, but it is enabled to convey the current, if it contain only faint traces of saline matter.

The following table will illustrate the manner in which saline

bodies may be classified in relation to their mode of electric decomposition; the *anion* indicating the electro-negative, the *cathion* the electro-positive component.

A, Simple . . .		Simple Anion . . . . Simple Cathion	Ag,Cl.
B, Complex .	I. Monobasic.	1. Simple Anion . . . . Compound Cathion	$H_4N,Cl.$
		2. Compound Anion . . . . . . Simple Cathion	$K,SO_4.$
		3. Compound Anion . . . . . . Compound Cathion	$H_4N,NO_6.$
	II. Polybasic.	1. Compound Anion . . . . . . Simple Cathions	$3\ Na,PO_8.$
		2. Compound Anion . . . . . . Simple and Compound Cathions .	$(Na,H,H_4N),PO_8.$

When *monobasic salts* are the subjects of electrolysis, the proportion of acid and of base is in single equivalents: thus, nitrate of potash yields 1 equivalent of potash and 1 of nitric acid for each equivalent of fused chloride of lead which is decomposed in the voltameter.

When a *polybasic salt* is submitted to electrolysis, for each atom of fused chloride of lead which is electrolysed in the voltameter, an atom of base appears at the platinode: for example, when 1 atom of the tribasic phosphate of soda is decomposed, 3 atoms of chloride of lead are reduced in the voltameter; and in the diaphragm cell Na_3,PO_8 yield $3\ NaO + 3\ H$ at the platinode, whilst $H_3PO_8 + 3\ O$ are liberated at the zincode. When the pyrophosphate of soda (Na_2,PO_7) is electrolysed, 2 atoms of chloride of lead are decomposed in the voltameter, whilst $2\ NaO + 2\ H$ make their appearance at the platinode of the diaphragm cell, and $H_2,PO_7 + 2\ O$ are set free at the zincode. When the metaphosphate of soda (Na,PO_6) is decomposed, 1 atom of chloride of lead is electrolysed in the voltameter, whilst $NaO + H$ appears at the platinode of the diaphragm cell, and $HPO_6 + O$ is liberated at the zincode. In each case the phosphoric acid thus transferred preserves its tribasic, dibasic, or monobasic character, according to the nature of the salt which was electrolysed.

The results of the electrolysis of the monobasic and polybasic oxysalts, it will thus be seen, admit of a simple explanation upon the binary theory. The results of the decomposition of the subsalts are not, however, so easily reconciled with this view. According to E. Becquerel, when basic salts (or subsalts) are decomposed,—for each atom of chloride of lead in the voltameter, 1 atom of acid

is liberated at the zincode, whilst all the atoms of base which were previously in combination with the single atom of acid are liberated at the platinode. My own experiments upon this point confirm this view, although from a numerous series of trials on the subnitrites, subnitrate, and subacetates of lead, I always obtained a smaller quantity of oxide of lead and of metallic lead than was required by theory, if this law held good; probably this deficiency was due to the secondary action of the solution upon the liberated oxide. When, for example, the triacetate of lead ($3\ PbO,C_4H_3O_3$) was decomposed, employing as the electrodes plates of lead instead of plates of platinum, for each atom of acetic acid and oxygen which appeared at the zincode, somewhat less than 1 atom of metallic lead and 2 atoms of oxide of lead appeared at the platinode: thus, the salt appeared to have undergone decomposition into $Pb + 2\ PbO$ and $C_4H_3O_4$. It is difficult to reconcile the idea of an ion consisting of $Pb + 2\ PbO$* with the binary theory. The most probable explanation appears to be this: viz., that the oxide of lead is attached to the neutral acetate in a manner analogous to water of crystallization, and that the neutral acetate is the true electrolyte, whilst the oxide is left upon the electrode in the insoluble form, as soon as the acid which kept it in solution is removed. A similar explanation may be applied to the case of other soluble subsalts.

Faraday's principle, 'that if the same pair of elements unite with each other to form more than one compound, it is only the compound which contains one atom of each element that admits of electrolysis' (Part I. p. 407), although generally true, cannot, however, be laid down as a law of electric decomposition. It occasionally happens that two different electrolytes containing the same elements exist. Both the chloride and the subchloride of copper, for example, are electrolytes. When a current of given strength is transmitted successively through, 1, a solution of sulphate of copper; 2, a solution of chloride of copper; and 3, fused subchloride of copper,—decomposition takes place simultaneously in each: but for each atom of sulphate of copper resolved into Cu and SO_4, one of chloride of copper is decomposed into Cu and Cl, and one of subchloride of copper into Cu_2 and Cl;—so that for each atom of copper separated at the platinode in the solution of

* E. Becquerel considered that he had obtained a new suboxide of lead by the electrolysis of its subsalts, but this appears to be an error. It is a mere mixture of metallic lead with oxide of lead, for the solution of neutral acetate of lead quickly dissolves the oxide and leaves the metallic lead; and the proportion of oxide to the metallic lead varies according to the nature of the salt operated upon.

the sulphate and the chloride, 2 atoms of copper are liberated from the subchloride.

If sulphate of copper be used as the measure of the voltaic action, Buff (*Liebig's Annal.*, cx. 257) considers when fused molybdic acid is electrolysed, that for each atom of sulphate of copper resolved into Cu and SO_4, 1 atom of molybdic acid (MoO_3) furnishes 1 atom of oxygen and 1 of MoO_2, and in like manner 1 atom of fused vanadic acid (VO_3) furnishes 1 of oxygen and 1 of VO_2. Fused bichromate of potash ($KO, 2\,CrO_3$) is also an electrolyte, and it is decomposed partially into K and CrO_4 and partially into Cr_2O_3 and O_3.

The same current which liberates 3 atoms of metallic copper from 3 of sulphate of copper, will resolve one atom of chloride of aluminum, (Al_2Cl_3), into Al_2 and Cl_3, 3 of subchloride of copper, 3 (Cu_2Cl), into Cu_6 and Cl_3, and 2 of chromic acid, 2 (CrO_3), into Cr_2O_3 and O_3.

(869) *Unequal transfer of Ions during Electrolysis.*—A curious circumstance in relation to the proportion in which the ions of the electrolyte travel towards the respective electrodes, was remarked in the course of these investigations on the decomposition of saline solutions. It was perhaps natural to expect that, if a solution underwent electrolytic decomposition for each equivalent of the compound decomposed, its component ions should be *transferred* to each electrode in the exact proportion of half an equivalent of each, although a whole equivalent was *liberated* in the manner shown at No. 2, in the scheme which follows:—

$$
\begin{array}{lrr|l}
 & & & \text{A} \\
(1) & & \text{Cu Cu} & \text{Cu Cu} \\
 & & SO_4SO_4 & SO_4SO_4 \\
\hline
(2) & -\text{Cu} \mid & \text{Cu}\quad \text{C} & \text{u}\quad \text{Cu} \qquad + \\
 & & SO_4\quad S & O_4\ SO_4 \mid SO_4 \\
\hline
(3) & -\text{Cu} \mid & \text{Cu} & \text{Cu Cu} \\
 & & SO_4 & SO_4SO_4 \mid SO_4 + \\
\hline
 & & & \text{A}
\end{array}
$$

In this scheme it is supposed that sulphate of copper is the electrolyte, each particle of copper represented by the symbol Cu being in combination with the particle of sulphion represented by SO_4 immediately beneath it. Let A A indicate the position of a diaphragm of bladder separating two equal quantities of the solution which in No. 1 are supposed to be in their normal state. Let No. 2 represent the same solution after it has undergone electrolysis; an equivalent of copper having been set free at the platinode, and one of sulphion at the zincode. It was not unnatural to expect that this result would have been attained by the transfer of half an equivalent

of copper into the division containing the platinode, whilst half an equivalent of sulphion passed towards the zincode, in the manner represented. Experiment, however, shows that such a supposition is erroneous, and that the decomposition more commonly happens in the mode represented in No. 3, in which case a whole equivalent of the anion is transferred to the zincode, leaving a whole equivalent of cathion uncombined, at the platinode. Sometimes when the oxide of a metal is soluble in water, the transfer of a small quantity of the cathion takes place towards the platinode, but the quantity of the cathion and the anion *set free* are always in equivalent proportions to each other (Daniell and Miller, *Phil. Trans.*, 1844, p. 16). Acids, whether they be soluble in water or not, always travel towards the zincode in proportions larger than the metals which are united with them pass towards the platinode.

D'Almeida (*Ann. de Chimie*, III. li. 257) attributes these remarkable irregularities, which occasion much inconvenience in electro-plating, to the development of free acid around the zincode. He considers that the acid, owing to its superior conducting power, conveys a large proportion of the current, and that the metal is then reduced upon the platinode by the hydrogen, at the moment of its liberation. He finds that when the solutions are strictly neutral the inequality of transfer is scarcely perceived. Strictly neutral solutions of copper and zinc, when decomposed between electrodes of copper or zinc respectively, become acid during the operation, because the metal at the zincode is not dissolved quite so rapidly as it is separated at the platinode, and consequently a little free acid accumulates around the zincode, and occasions the irregularity in transfer of the ions which we are now considering. When a current traverses a saline solution kept constantly acid in the zincode cell, whilst the platinode is maintained constantly neutral, the salt is transferred unequally, the zincode becoming least impoverished; but if the solution be kept neutral around the zincode whilst it is maintained alkaline around the platinode, the result is reversed, and the impoverishment of the platinode is the least marked.

The explanation of D'Almeida is confirmed by the subsequent researches of Magnus. Hittorf (*Pogg. Annal.*, lxxxix. 177, and xcviii. 1) gives a different, and, as it appears to me, an improbable and complicated theory for the explanation of these results; but his experiments appear to be consistent with those already quoted.

(870) ***Electrovection,*** or ***Electrical Endosmose.***—It was observed many years ago by Porrett, when water was placed in a diaphragm

apparatus, one side of which was connected with the positive, and the other side with the negative electrode of the battery, that a considerable portion of the liquid was transferred from the positive towards the negative side of the arrangement. It has since been found that the same result occurs in a minor degree when saline solutions are electrolysed, and generally the greater the resistance which the liquid offers to electrolysis the greater is the amount which is thus mechanically carried over. From numerous experiments I have found that in all these cases the water carries with it a proportion of the salt which it holds in solution. It appears from the researches of Wiedemann (*Poggendorff, Annal.*, lxxxvii. 321), that the amount of liquid transferred, *cæteris paribus*, is proportioned to the strength or intensity of the current; that it is independent of the nature and thickness of the diaphragm by which the two portions of liquid are separated; and that when different solutions are employed, the amount transferred in each case, by currents of equal intensity, is directly proportional to the specific resistance of the liquid.

When more than one salt is present in a solution, the current, when below a certain strength, decomposes only one of them, the best conductor being decomposed when the current is feeble; but when the intensity of the current passes a certain limit, a portion of the inferior conductor experiences decomposition. This limit to the intensity of the current, according to Magnus (*Poggend. Ann.* cii. *loc. cit.*), varies with the size of the electrodes, and with the distance between them, as well as with the proportion in which the different electrolytes are mixed.*

(871) *Secondary Results of Electrolysis.*—The explanation already given of the mode in which the oxysalts are electrolysed was happily applied by Daniell to the elucidation of the origin of the voltaic power, in a combination contrived by Becquerel (230), which presents many interesting peculiarities. If a porous tube filled with nitric acid be plunged into a vessel containing a solution of potash, and the wires of a galvanometer, armed with platinum plates, be plunged one into the nitric acid, and the other into the alkaline solution, a current will circulate; oxygen will be emitted from the plate immersed in the potash, and nitrous acid, owing to the absorption of hydrogen by the nitric acid, will be

* The results obtained by Magnus upon the decomposition of iodic acid, bichloride of tin, and some other bodies, appear to be only secondary actions, not produced by the direct electrolysis of these compounds, and consequently they do not admit of being applied to the general theory. This, indeed, has already been pointed out by Buff.

formed around the other plate, whilst nitrate of potash is slowly produced by transudation of the two liquids through the pores of the diaphragm. By connecting several of these cells together in succession, upon the principle of the ordinary battery, the power may be considerably augmented. The decomposition which appears to occur is represented by the following symbols, in which H,NO_6 indicates the nitric acid, and KO the potash: the position of the brackets above the symbols indicates the arrangement before the current is established, whilst, after its passage, the arrangement is supposed to be that indicated by the brackets beneath:—

$$\overbrace{H,NO_6}\ \overbrace{H,NO_6}\ \Big|\ \overbrace{K,O}\ \overbrace{K,O}$$

It is particularly to be observed that no development of oxygen or of hydrogen occurs upon the platinum plates until the two plates are united by a conducting wire, and it ceases as soon as the conducting communication between the plates is interrupted: in the latter case the polar arrangement of the particles is interfered with, although the process of combination between the potash and the nitric acid continues. The secondary action of the nitric acid on the hydrogen which is set free is necessary to the development of the current. If sulphuric acid be substituted for the nitric, the hydrogen is not absorbed, and no current is obtained, probably because it is neutralized by the counter current which the accumulation of the hydrogen upon the platinum plate tends to produce (231).

The secondary actions of the voltaic current are often of great importance; they require to be carefully distinguished from its primary effects. Secondary results are, in some instances, produced by the action of the liberated components of the electrolyte upon the materials employed as electrodes: thus, if a slip of copper be substituted for one of platinum, as the zincode of the battery, and be immersed in diluted sulphuric acid, sulphate of copper will be formed by the combination of the copper with the disengaged sulphion. At other times, the secondary results are manifested by the reaction of the ion upon the liquid in which the electrolyte is dissolved, as when the potassium or sodium, set free at the platinode in an aqueous solution of its salts, liberates hydrogen by removing oxygen from the water. In the cases just cited, the affinities of the disengaged ions are very intense, and the secondary action is exactly proportioned to the primary, so that it may be employed as a measure of the current: but when the tendency to combination is more feeble, the proportion

of these secondary actions to the primary one is greatly influenced by the extent of surface exposed by the electrode to the liquid, and the energy of the current, and consequent quantity of the ion disengaged at once. Generally, the slower the action, and the larger the surface of the electrode, the more uniform and complete is the secondary action. These results are well exemplified by Bunsen's researches on the isolation of the more oxidizable metals by the voltaic current. If a thin platinum wire be used as the platinode in a solution of chloride of chromium, to convey the current from 4 or 5 cells of the nitric acid battery, metallic chromium may be obtained without difficulty; but if a plate of platinum be employed,—oxide of chromium, mixed with a certain amount of hydrogen, is liberated; in the latter case the metal has time to decompose the water before fresh particles of chromium are deposited upon its surface.

In consequence of these secondary actions, the same element may sometimes appear at one electrode, sometimes at the other, as is seen in the case of nitrogen: if, for instance, a solution of sulphate of ammonia be submitted to electrolysis, it yields hydrogen at the platinode, and a mixture of nitrogen with oxygen is set free at the zincode. The nitrogen in this case is liberated as a secondary result of the combination of a portion of the oxygen with the hydrogen of the ammonia. If nitrate of ammonia be substituted for the sulphate, nitrogen appears among the gaseous products at both electrodes, the nitric acid being deprived of its oxygen by the hydrogen evolved at the platinode, and the ammonia of its hydrogen by the oxygen set free at the zincode.

If a solution of acetate of lead be employed as the electrolyte, the acetic acid undergoes partial decomposition from the action of the oxygen upon it at the moment of its liberation at the zincode, but at the same time a portion of the oxygen also enters into combination with some of the oxide of lead contained in the liquid, and, as Warington proved, a deposit of peroxide of lead is produced. Nobili, who first observed this phenomenon, found that if a polished steel plate be employed in such a solution as the zincode to the battery (4 or 6 cells of Grove's may be employed), the deposit assumes the form of a thin film, which exhibits the iridescent tints of Newton's scale,—the tints varying according to the thickness of the film produced. Other experimentalists have modified the patterns which may be obtained by these *metallochromes*, which have even been applied by Becquerel to the imitation of the tints of flowers; and by varying the strength of the battery and of the solutions employed, he has succeeded in producing some effects of

great delicacy and beauty. Salts of manganese or of bismuth may be substituted for those of lead, with similar results.

Many of these secondary actions are very interesting: Kolbe has devoted particular attention to the effects of oxygen when liberated during electrolysis (*Proceed. Chem. Soc.*, iii. 285, and *Q. J. Chem. Soc.*, ii. 157). Hydrochloric acid, especially when previously mixed with sulphuric acid, is in this manner partially converted around the zincode into chloric and perchloric acids; and in an acid solution of chloride of potassium, chlorate and perchlorate of potash are formed. Cyanide of potassium in solution, when subjected to the voltaic current, is in like manner converted into the cyanate. A concentrated solution of chloride of ammonium evolves hydrogen at the platinode, but the chlorine, instead of being liberated at the zincode, acts upon the chloride of ammonium, and forms oily drops of chloride of nitrogen, which explode when touched by the opposite electrode. Smee has shown that by means of the voltaic current the yellow prussiate may be converted into the red prussiate of potash. Kolbe has, further, ascertained the effect of the liberated oxygen upon various organic compounds, and by submitting valerate of potash to electrolysis he decomposed the valeric acid ($HO,C_{10}H_9O_3$) which it contains, and succeeded in obtaining from it a new substance, *valyl* $(C_8H_9)_2$, (or more properly *tetryl*); a new ether, $(C_8H_9O)_2$, *tetrylic ether*, and a hydro-carbon (C_8H_8), apparently identical with oil gas (405): and by a similar process from acetic acid ($HO,C_4H_3O_3$) he obtained methyl $(C_2H_3)_2$, the homologue of tetryl. Particular interest is attached to these researches, owing to the circumstance that in each case the compounds obtained by the electrolysis belong to a series related to an alcohol different from that which was submitted to decomposition. The valeric acid thus yields an ether of the tetrylic series; and acetic acid, which is a derivative of wine alcohol, furnishes the hydrocarbon which belongs to the wood spirit series.

(872) *Nascent state of Bodies.*—It is obvious, from the powerful effect which oxygen produces at the moment of its liberation from compounds during electrolytic decomposition, that such oxygen must be in a condition very different from that in which it exists when once it has assumed the gaseous form. Oxygen is not insoluble in water, and it is therefore possible to bring it in small quantities at a time into chemical contact with salts or other bodies which water may hold in solution. Oxygen gas may, however, be transmitted for an unlimited time through a solution of chloride of potassium without effecting the conversion of any portion of the chloride into chlorate, or into perchlorate of potash;

and yet, as has been mentioned in the foregoing paragraph, this change is easily effected by oxygen as it escapes during the electrolysis of an acidulated solution of the chloride of potassium. But it is not necessary that oxygen should be liberated by the agency of the voltaic battery in order that it should acquire this increase of activity. If hydrated protoxide of nickel, or protoxide of cobalt, be suspended in a solution of potash, it will undergo no change when subjected to a current of oxygen gas; but if a current of chlorine be substituted for the oxygen, the whole of the metallic oxide will be converted into a brown sesquioxide: this change arises from the action of the chlorine upon the potash, during which, chloride of potassium is formed, whilst oxygen is set free, and, at the moment of its liberation, attaches itself to the oxide of nickel or of cobalt; $KO,HO + Cl + 2\ (NiO,HO) = KCl + Ni_2O_3,\ 3\ HO$. Other substances besides oxygen exhibit this peculiarity, and chemists have long recognised the fact, that bodies, when in this *nascent state*, that is to say, when in the act of liberation from other substances, display more energetic affinities than they show when once obtained in the isolated form:—For example, cyanogen and chlorine do not enter directly into combination; but if cyanogen at the instant that it is set free from another compound, be presented to chlorine, the two bodies combine; thus, if moist cyanide of mercury be decomposed by means of chlorine, chloride of cyanogen may be obtained: the chlorine removes the mercury step by step, and the cyanogen, at the moment of its liberation, enters into combination with another portion of chlorine. In a similar manner, sulphur, when set free from an alkaline persulphide in the midst of a solution of hydrochloric acid, combines with hydrogen, and forms persulphide of hydrogen, $KS_5 + HCl = KCl + HS_5$, the chlorine taking the potassium, whilst the sulphur and the hydrogen, both in the nascent state, unite to form a new compound, although their affinity is so slight that this compound separates spontaneously into sulphuretted hydrogen and free sulphur. The process of double decomposition is particularly applicable in cases where the mutual affinity of the bodies which it is desired to obtain in combination is comparatively feeble. It is not impossible that this superior chemical activity of bodies in the nascent state may arise from the fact that their particles are individually electrified at the moment of their separation from a previous state of combination; and that in this condition they may exert upon the particles of dissimilar contiguous matter, a force of induction which may be the agent that determines their chemical combination: if by a process of *double* decomposition the particles

of both compounds were oppositely electrified, combination might be expected to be proportionately facilitated:—For instance, if a solution of sulphide of potassium and one of chloride of copper be mixed, they will decompose each other, the sulphur being negative, will tend to combine with the positive copper, and the positive potassium will unite with the negative chlorine. If the brackets in No. 1 represent the mode in which the molecules are arranged on the instant of mixture previous to decomposition, those in No. 2 will illustrate the arrangement of the molecules after mutual decomposition has been effected:—

$$(1)\ \begin{array}{c} \overbrace{\overset{+}{\mathrm{K}}\ \overset{-}{\mathrm{S}}}\ \overbrace{\overset{+}{\mathrm{Cu}}\ \overset{-}{\mathrm{Cl}}} \\ \underbrace{\underset{-}{\mathrm{Cl}}\ \underset{+}{\mathrm{Cu}}}\ \underbrace{\underset{-}{\mathrm{S}}\ \underset{+}{\mathrm{K}}} \end{array} \text{ become } \left\{\begin{array}{c} \overset{+}{\mathrm{K}}\ \overbrace{\overset{-}{\mathrm{S}}\ \overset{+}{\mathrm{Cu}}}\ \overset{-}{\mathrm{Cl}} \\ \underset{-}{\mathrm{Cl}}\ \underbrace{\underset{+}{\mathrm{Cu}}\ \underset{-}{\mathrm{S}}}\ \underset{+}{\mathrm{K}} \end{array}\right\}\ (2)$$

(873) *Theory of the Electrical Origin of Chemical Affinity.*—It has already been remarked (214, 225) that whenever two dissimilar substances, electrically insulated, are brought into contact, and are separated from each other, disturbance of their electrical equilibrium is produced; one of the bodies becoming negatively electrified whilst the other indicates a corresponding charge of positive electricity. It is a well ascertained fact, that certain substances, by friction, acquire one kind of electricity more readily than the other; thus, for example, sulphur, when rubbed upon flannel or fur, becomes negatively electric, whilst glass, on the other hand, most readily assumes the positive state. What has been proved to occur when masses of matter are brought into contact was supposed by Davy (*Phil. Trans.*, 1807), to happen also when the molecules of two dissimilar substances are brought within the sphere of mutual activity; he assumed 'that, chemical and electrical attractions depend upon the same cause, acting in one case on particles, in the other on masses of matter' (*Phil. Trans.*, 1826, p. 389); and all the phenomena of chemical affinity have been referred to the exertion of mutual electrical attraction between the atoms of each substance in the compound. When, for example, chlorine and potassium are united, it is supposed that each atom of chlorine, by contact with an atom of potassium, becomes negatively electrified, whilst the potassium becomes positively excited; a certain portion of the positive electricity from the chlorine uniting with a corresponding amount of negative electricity which is liberated from the potassium, thus producing the light and heat which attends the combination of these two bodies (Berzelius). Sup-

posing each atom of both kinds of matter to be associated with equal quantities of both electricities, and that the two different electricities be represented by the signs + and −, we may represent the potassium and chlorine by symbols; (− K +) indicating an atom of potassium, and (−Cl +) an atom of chlorine. As soon as the two bodies are brought into contact, it is supposed that the chlorine loses a certain amount of positive electricity, whilst the potassium loses an equal quantity of negative electricity, the change being symbolized thus (+KCl−) and (+ −). When the chloride of potassium is decomposed electrolytically, a quantity of positive electricity is transferred from the positive wire of the battery to the chlorine, and compensates for that which it has lost; and when this amount of electricity has been restored, the chlorine no longer has any tendency to remain in combination with the potassium, and hence it is set free upon the positive plate, whilst a simultaneous transfer of negative electricity to the potassium occurs from the negative plate, and the alkaline metal is therefore liberated upon the negative side of the arrangement. The electricity which is set free by the battery is supplied by the action of the sulphion upon the zinc, in the cells of which the battery consists.

The remarkable law discovered by Faraday, that the same current of electricity when transmitted successively through various electrolytes, decomposes each in the proportion of their respective chemical equivalents (247, 4) adds greatly to the probability of the supposition that electrical and chemical phenomena are due to different manifestations of the same agent. So strong was Daniell's conviction upon this point, that he applied the term *current affinity* to the voltaic current; since by means of the proper application of conductors, or channels for the force, the chemical affinity of a portion of zinc and sulphuric acid at one point could be transferred to a distant spot, and could there be made to effect an equivalent amount of chemical decomposition upon a different compound. The chemical equivalent of any substance upon the electro-chemical theory, is that quantity of each body which is associated with an amount of electricity equal to that associated with a given weight of some substance, such as hydrogen, which is selected as the standard of comparison; the proportion of electricity which is associated with a given weight of any substance being inversely as its atomic weight. Assuming the specific electricity of hydrogen to be represented by the arbitrary number 1000, the following is given by Daniell (*Introd. to Chem. Phil.*, 2nd Ed. p. 687) as an approximative table of the *specific electricity* (or

quantity of electricity associated with *equal weights*) of a few of the more important elements and compounds:—

Cathions.	Equivalent.	Specific Electricity.	Anions.	Equivalent.	Specific Electricity.
Hydrogen . .	1·0	1000	Oxygen . . .	8·0	125
Potassium . .	39·2	25	Chlorine . . .	35·5	27
Sodium . . .	23·3	43	Iodine . . .	126·0	8
Zinc	32·5	31	Bromine . . .	78·3	12
Copper . . .	31·6	31	Fluorine . . .	18·7	55
Ammonia . .	17·0	58	Cyanogen . .	26·0	38
Potash . . .	47·2	21	Sulphuric Acid .	40·0	25
Soda	31·3	32	Nitric Acid . .	54·0	18
Lime	28·5	35	Chloric Acid .	75·5	13

Ingenious, however, as is the electrical theory of chemical affinity, it must be admitted that it is far from being free from objection and difficulty when it is attempted to apply it to all cases of chemical action. It has been already stated that a very large number of bodies exist which are not susceptible of electrolysis. Indeed, the chief classes of electrolytes are: 1, binary compounds of the non-metallic elements with the metals, such as the oxides, chlorides, iodides, bromides, and fluorides; 2, compounds of bodies like cyanogen with the metals, such as the cyanides and the sulphocyanides; and 3, compounds of the metallic oxides with the oxyacids, such as the nitrates, sulphates, borates, carbonates, acetates, tartrates, &c. Now, so long as a compound consists of two elements only, if it be decomposed at all, there is no difficulty in anticipating the result of the voltaic action;—the electro-negative element will appear at the zincode, and the electro-positive element at the platinode; yet there are binary compounds which are not electrolysable, such, for instance, as pure water, and chloride of sulphur. If their particles be united by electric opposition, why should they not yield to the current? In the case of more complex bodies, such, for example, as nitrate of silver, or borate of lead, it is not possible, *à priori*, to say how the compound would yield under the electric influence. It is quite clear in the case of a salt, that the power which holds together the two ions of the salt in the form of two *iso-electric* groups (or groups of equal electric energy), must be of a different order from that which holds the elements of its component ions in combination. The tie which binds together nitrate of silver as Ag,NO_6, must be of an order different from that which unites the elements of *nitrion* (NO_6) together. Sulphate of soda, again, as an electrolyte is separated into Na and SO_4. But neither nitrion nor sulphion can exist in the separate form; how can they become associated under electric

influence? Again, $(SO_3)_2$, sulphuric anhydride, is not an electrolyte when fused: the same thing may be said of fused boracic anhydride; and examples of this kind might be multiplied almost without limit. Why, if chemical affinity be due to the exertion of electric action, should certain bodies be readily decomposable by the voltaic current, and why should others of less complex composition, resist it entirely? At present, no hint appears to have been given which offers any clue to the solution of these questions.

Practical Applications of Electrolytic Action.

(874) *Electrotype, Voltatype, or Galvano-Plastics.*—Shortly after Daniell had invented his constant battery, he observed that copper deposited upon a plate of platinum furnished a coherent sheet, in which the lines and irregularities on the surface of the platinum were faithfully reproduced upon the deposited copper; but he made no practical application of the observation. In the year 1839, Jacobi, of St. Petersburg, announced that he had discovered a method of making exact copies of a metallic surface in copper by means of the voltaic battery, and shortly afterwards Messrs. Spencer and Jordan, who had each independently arrived at a similar result, published the methods which they had employed for the attainment of this object. The processes thus disclosed were so simple and easy of execution that they were immediately repeated with success; and in the following year Mr. Elkington in England, and M. Ruolz in France, began to apply the voltaic battery on an extensive scale to the arts of plating and gilding. Since this period the voltaic battery has been most extensively employed as a means of depositing not only copper, gold, and silver from their solutions, but zinc, tin, lead, platinum, and nickel: many other metals have also, for particular purposes, been reduced from their salts by its means.

For the deposition of metallic copper, a solution of the sulphate of this metal is employed, but the mode of using it varies with the object in view. Suppose that it be desired to obtain a copy of an engraved copper plate: a wire or slip of copper having been soldered to the plate for the purpose of facilitating its connexion with the battery, the back of the plate is covered with a resinous varnish, by which means this surface is electrically insulated from the solution, and it is thus protected from any deposit of reduced metal. The plate thus prepared is connected with the negative electrode of a voltaic battery, consisting of 3 or 4 of Smee's or Daniell's cells, and immersed vertically in a bath consisting of a saturated solution

of sulphate of copper. A sheet of copper, equal in size to the one to be copied, is suspended parallel to the latter in the liquid, and connected with the positive electrode of the battery; an immediate decomposition of the solution ensues; metallic copper is deposited upon the entire surface of the negative plate, in the form of a coherent, continuous sheet, and a nearly corresponding amount of copper is dissolved from the positive plate, so that the liquid remains constantly charged with a quantity of sulphate of copper, approximatively equal to that originally employed. At the commencement of the operation, care must be taken to ascertain that the deposit occurs uniformly over the whole surface of the negative plate, for if any portion of it be soiled by grease or resinous matter, the copper will not be thrown down upon those parts; when once the deposition has commenced uniformly, it goes on without difficulty. If the plates be suspended vertically, the solution should be frequently agitated, for unless this precaution be taken, the liquid around the negative plate becomes impoverished, whilst that around the positive plate becomes unduly saturated with the copper salt (869); currents are then produced in the liquid, owing to its unequal density, and they occasion the formation of vertical grooves and striæ upon the back of the sheet of deposited metal. This inconvenience is sometimes obviated by supporting the two plates in the bath in a horizontal position, the negative plate being undermost; the positive plate must in this case be enveloped in flannel, in order to prevent the small particles of metal, which are constantly being detached from it, from falling upon the lower plate, and interfering with the regularity of the deposition.

The deposit varies in hardness and coherence according to the number of cells employed in the battery, the relative size of the plates of the battery and those of the depositing cell, and the temperature and degree of concentration of the solution. The more slowly the action takes place if the solution be concentrated, the harder and more crystalline is the deposit. By modifying the power of the battery, and the strength of the solution, in the manner which experience soon indicates, copper may be obtained of any desired degree of toughness.

When the deposit has acquired the necessary thickness, it is detached at its edges from the original plate, and can then be stripped off without difficulty. The thin film of oxide, or of other adhering impurity, derived from the exposure even of a freshly deposited copper plate to the air for a few hours, is sufficient to prevent too intimate an adhesion between the plate and the de-

posit. In the electrotype thus obtained, the lines which are cut away upon the surface of the original plate are represented in relief in the copy, and if a fac-simile of the engraving be desired, a new deposit must be formed upon the copy thus procured; in this second transfer, an exact duplicate of the original engraving will be presented. Many large and valuable copper plates, amongst which are some of those engraved for the Art Union, have been thus multiplied with success. So faithfully does the deposit reproduce all irregularities upon the surface of the matrix on which it is deposited, that copies of daguerreotype plates have been obtained by its means, in which the original design is accurately transferred to the deposit of copper, without destroying the original impression.

(875) *Preparation of Moulds for Electrotyping.*—In copying medals or other works of art, it is frequently necessary to employ casts of the objects, instead of the original objects themselves, which might be liable to injury by immersion in the metallic solution. These casts may be made in fusible metal, or in stearine, in plaster, or gutta percha. Gore (*Pharm. Journal*, July, 1855) recommends a mixture of 2 parts of gutta percha and 1 part of marine glue; the materials are to be cut up, and the glue melted at a gentle heat and incorporated with the gutta percha. The paste is to be applied whilst soft, with a pressure gradually increasing, to the surface of the medal, or other object which it is desired to copy. In certain cases an impression of the object to be copied is obtained in sheet lead by the application of strong pressure. In every instance before proceeding to effect the metallic deposition, the back of the mould, if made of metal, or of a conductor of electricity, must be coated with a resinous varnish, or with some non-conducting matter. When moulds of plaster of Paris are employed they must be rendered impervious to moisture by immersion in melted wax or tallow; after which the surface to be copied is endued with the power of conducting electricity, by applying finely powdered black-lead, of good quality, to the surface by means of a brush; taking care that every portion of the surface to be copied is completely coated by it. The cast is then connected with the negative wire of the battery by means of a strip of sheet lead, or a copper wire, which is in electric contact with some portion of the black-lead surface. Impressions of seals in sealing wax, stamps in relief upon pasteboard or paper, and the engraved blocks used for wood-cuts, thus rendered conductors upon the surface, may be electrotyped with facility. Even glass may be rendered a conductor by the use of one of the methods of depositing silver

upon its surface (793). Leaves, flowers, fruits, and insects have also been coated with copper, or with silver, by the electrotype process. A mode of producing a conducting surface upon these articles, due to Capt. Ibbetson, consists in immersing them in a weak solution of phosphorus, either in bisulphide of carbon or in ether, allowing the solvent to evaporate from the surface, and then plunging the objects into a solution of nitrate of silver; the phosphorus left upon the surface reduces a very thin film of silver upon the superficial portions of the objects, sufficient to enable them to receive the deposit from the battery, if they be properly connected with the negative wire, and submitted in a metallic bath to the action of the electric current. Steel plates cannot be copied by immersing them in a bath of sulphate of copper, because the steel and the sulphate act chemically on each other, and thus the engraving would be destroyed. This difficulty has been overcome by electrotyping them first in silver, which can be deposited upon the steel without injury, and upon this silver matrix a copper fac-simile of the original plate can afterwards be obtained.

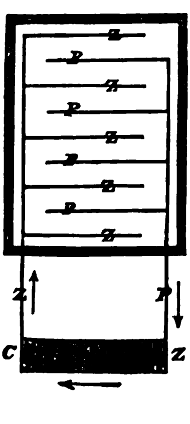
For the electrotyping of small objects, such as coins or medals, it is not necessary to use a separate voltaic battery, since the depositing cell itself may, in the following manner, be converted into a voltaic couple of sufficient power to decompose the sulphate of copper:—Let a glass cylinder, such as the chimney of an argand gas-burner, be closed below by a plug of plaster of Paris, and be supported in a vessel containing a solution of sulphate of copper, in which the mould or the medal to be copied is supported by a metallic wire; let the inner tube be filled with sulphuric acid diluted with 10 or 12 times its bulk of water, and let an amalgamated zinc rod be placed in its axis. If this zinc rod be connected with the wire proceeding from the mould of the medal to be electrotyped, copper will be deposited upon the surface of the mould. The apparatus in fact constitutes a cell of Daniell's battery, with a trifling modification in its form. The solution of copper should be maintained uniformly saturated with sulphate of copper, by suspending crystals of the salt in the upper part of the liquid.

(876) *Electro-zincing.*—Zinc may be deposited from its sulphate on the surface of iron, by processes similar to those used for sulphate of copper. The operation requires but a feeble current, and admits of being performed upon a very large scale: the iron links of the Charing Cross suspension bridge, which are passed into the abutments on the side of the river, were successfully submitted to this operation; each of these links is 24 feet in length, and of proportionate width.

It is not possible, however, to obtain coherent plates of all the metals with the same facility as is the case with copper and zinc. Many of the metals are thrown down from their solutions in a crystalline form, whether the deposition be effected rapidly or slowly. Silver is separated thus from its nitrate, and lead exhibits a similar deportment when the acetate or the nitrate of this metal is electrolysed. Gold and platinum do not give coherent plates when solutions of the chlorides of these metals are submitted to voltaic decomposition. Lead may be deposited upon iron from a solution of oxide of lead in potash; and a solution of oxide of tin in potash may be used to obtain coherent plates of tin by electrolysis. In like manner ammoniacal solutions of the salts of cobalt and nickel may be employed to furnish electrotype plates of these metals. In some cases, however, where a simple salt fails to give a satisfactory result, the effect may be obtained by the employment of certain double salts of the same metal with potassium or with sodium: thus the double cyanide of gold and potassium is largely employed for gilding, and the corresponding salt of silver is extensively used in electro-silvering. In gilding, silvering, and zincing, one great desideratum is to obtain a firm adherence between the newly deposited metal and the object to be gilt or plated; the surface of the metallic object is therefore first rendered *chemically* clean, a result which is carefully avoided in the process of electrotyping. In the latter case it is usual to expose the object, if freshly polished, to the atmosphere for 24 hours before placing it in the depositing cell, in order to prevent permanent adhesion.

(877) *Electro-Plating.*—The metals upon which an adherent coating of silver is most readily deposited are brass, copper, bronze, and German silver; but it may also be effected on steel. The articles to be plated are cleansed from adhering greasy matters either by boiling them in a weak alkaline solution, and then washing; or they are heated to low redness in a muffle: in either case they are next dipped into diluted nitric acid for the purpose of removing any adhering film of oxide. They are then brushed with a hard brush and some sand; and having been rinsed from adhering impurities, and separately attached to a clean copper wire, they are again dipped for an instant into nitric acid, washed, and immersed whilst still wet in the silvering bath. Let fig. 349 represent a plan of this bath, and c z the voltaic battery; the copper wires

Fig. 349.



attached to the articles to be plated are twisted round the rods P P P, which are connected with the negative wire of the battery, whilst the positive wire is connected with a series of silver plates, Z Z Z, which are also immersed in the silvering liquid. This solution is commonly prepared by dissolving cyanide of silver in a solution either of cyanide or of ferrocyanide of potassium. Solutions containing hyposulphite or sulphite of silver are occasionally employed. In order to prepare the silvering bath, a solution of nitrate of silver may be precipitated by the addition of cyanide of potassium so long as it produces a precipitate; this precipitate, after having been washed by decantation, is dissolved in a solution of cyanide of potassium. An excess of cyanide of potassium is requisite; at least 3 parts of cyanide of potassium being employed for 1 part of cyanide of silver.* A solution which contains $\frac{1}{30}$th of its weight of silver is found to be of a convenient strength for ordinary operations. When cyanide of potassium is used in the bath as a solvent, the solution gradually becomes alkaline from the formation of carbonate of potash, which accumulates in the liquid and interferes with the regularity of the decomposition: but if cyanide of calcium be substituted for the cyanide of potassium, this inconvenience is obviated, since carbonate of lime is formed, and owing to its insolubility, it sinks to the bottom of the bath as fast as it is produced. The articles when plated have a dead white or chalky surface, but they may be burnished by pressure if desired, and they then assume the brilliant lustre of polished silver. It is remarkable that the addition of a very small proportion of bisulphide of carbon to the bath causes the deposited silver to assume the lustre of the polished metal.† The amount of silver which is deposited can be regulated very accurately by weighing the articles before immersion, and weighing them again afterwards. A deposit of from 1¼ ounce to 1½ ounce of silver to a square foot of the plated surface answers well in practice; the sheet of silver under these circumstances being of about the thickness of ordinary writing paper. The solution must

* If ferrocyanide of potassium be used as a solvent of the cyanide of silver, 10 parts of this salt are required for the solution of 1 part of cyanide of silver.

† In order to effect this object, 6 ounces of bisulphide of carbon are directed to be agitated with 1 gallon of the plating liquid, and set aside for 24 hours. Two ounces of the liquid thus obtained, are to be added over night to 20 gallons of the ordinary plating liquid; the bath is ready for use next morning. This addition of the solution of the bisulphide requires to be renewed daily, to make up for the loss of the bisulphide of carbon by evaporation. Much care is required in the use of such a solution, for it is liable to changes which are produced by very slight modifications in the mode of working.

be frequently stirred in order to preserve the liquid of uniform density and composition throughout.

The batteries used at Birmingham for gilding and silvering are in general simply plates of amalgamated zinc opposed to plates of copper in diluted sulphuric acid : the plates are so arranged that they can be readily raised or lowered in order to expose a smaller or larger surface to the action of the acid. The superficial area, and number of the plates used, are made to vary according to the size and nature of the objects to be operated upon. The workman judges from experience as to the number of pairs to be employed; it seldom happens that more than two or three pairs of plates are needed. In Paris, Bunsen's carbon and zinc batteries are also employed with success in these operations.

(878) *Electro-Gilding and Platinizing.*—It is possible to gild most of the ordinary metals by voltaic action. Articles which consist of brass, bronze, copper, or German silver are first annealed, then *pickled*, as the operation of immersing them into the mixture of diluted nitric and sulphuric acids is termed, after which they are scrubbed and 'dipped' in strong nitric acid, and then rinsed in water, as is practised in preparing them for plating. Silver articles are cleansed in a similar manner, but they do not require to be 'dipped.' Iron and steel may be gilt by cleansing them from grease, first with potash, and then by dipping in nitric acid, and scouring the surface with burnt clay finely sifted, in order to remove the black stains produced by the liberation of carbon. A more powerful current is required for gilding upon iron than upon the metals previously mentioned.

The gilding bath most usually employed, consists of cyanide of gold dissolved in cyanide of potassium. It may be prepared by dissolving gold in aqua regia, and adding cyanide of potassium to the diluted liquid so long as it produces a precipitate; a brisk effervescence accompanies the action, and a yellow deposit of protocyanide of gold (AuCy) is formed: the clear liquid is decanted, and the precipitate is redissolved in a solution containing between 7 and 8 parts of the cyanide of potassium to 1 part of gold: the solution is then diluted until 100 parts of the liquid contain 1 part of gold.

M. Ruolz has shown that various other gilding baths may be used instead of the double cyanide of gold and potassium: for example, he finds that the cyanide of gold may be employed when brought into solution by the ferrocyanide, or by the ferridcyanide of potassium; he has also used with success the double sulphite of gold and soda, the solution of the double chloride or iodide of

gold and sodium with an excess of soda, and even the sulphide of gold dissolved in a neutral solution of protosulphide of potassium.

As yet the voltaic deposition of platinum has not been practised to any considerable extent; it is stated, however (*Comptes Rendus*, vol. xiii., p. 1013), that a solution of the double chloride of platinum and potassium in caustic potash may be applied to this purpose with tolerable success.

§ IV. Influence of Light on Affinity—Photography.

(879) *Influence of Light upon Crystallization.*—It is a familiar observation, that volatile bodies which crystallize as they are condensed after spontaneous sublimation,—such as camphor, naphthalin, and sesquichloride of carbon,—if placed in glass vessels, collect upon the side of the glass which is exposed to the light, whilst no crystals are deposited upon the other side of the vessels. This effect, however, is not confined to crystallizable substances. If a few drops of water be placed at the bottom of a bottle, the sides of which are kept dry, and the mouth of the bottle be closed, on placing it in the sunshine for a few minutes a deposit of globules of moisture will speedily take place upon the illuminated sides of the bottle. A similar effect is often seen in the vacuum of a barometer, globules of mercury being condensed upon the side of the tube which is exposed to light. Draper (*Chemistry of Plants*, Appendix, p. 124) has made a number of observations on these phenomena, from which it appears that the transmission of light through an aperture in a metallic screen, or the reflection of the light from a surface of glass, and other apparently trifling modifications of the light, will prevent the deposition of vapour in such cases. The whole subject is well worthy of further investigation.

(880) *Chemical Actions of Light.*—The rays of the sun are not only the great source both of heat and light to the globe which we inhabit, but they are constantly exerting upon the various substances upon its surface, a chemical influence of the utmost importance to the existence of animal and vegetable life, and to the permanence of the present order of creation. The occurrence of this remarkable chemical activity in the solar rays may be shown in various ways:—When perfectly dry chlorine is mixed in the dark with hydrogen, no chemical change takes place; if the two gases have been exposed separately to the beams of the sun, and have subsequently been mixed in the dark, they may be preserved in this condition also without change, so long as they are screened

from the light; but if the mixture be exposed to diffused daylight, it will be observed that the two gases begin gradually to combine, and if they be free from admixture with uncombined oxygen or excess of hydrogen, sudden combination with explosion occurs when they are exposed to the direct rays of the sun. The rapidity with which this combination occurs is proportioned to the intensity of the light, and an instrument for measuring the amount of the action which is produced by diffused daylight, was described by Draper, under the somewhat fanciful name of the *tithonometer* (*Phil. Mag.*, Dec. 1843).

(880 *a*) *Photo-chemical Induction.*—An elaborate investigation of the circumstances which influence the action of light upon a mixture of chlorine and hydrogen, by Bunsen and Roscoe, will be found in the *Phil. Trans.* for 1857.

From these investigations it appears to be probable that a species of induction precedes the chemical action. It was found by Draper that on exposing the explosive mixture of chlorine and hydrogen to diffused daylight, the amount of condensation gradually increases for a few minutes, until it attains a maximum, at which point the rate of combination between the two gases continues to be uniform for equal amounts of incident light. Draper attributed this slow attainment of the maximum rate, to an effect of light upon chlorine alone, in consequence of which it was gradually converted into a new and more active modification. Bunsen and Roscoe, however, did not find that either chlorine or hydrogen, when separately exposed to light, exhibited, after they had been mixed and again exposed, any action different from that observed when the gases were prepared and mixed in the dark and then exposed to light; they consider that the light acts by overcoming certain resistances which oppose the combination of the two gases; and this peculiar action they term *photo-chemical induction.* The time which elapses before the maximum action, due to the light, is attained, varies considerably in different experiments,—ranging from 3 or 4 minutes up to 10 or 15. The more intense the light, the more rapidly is the maximum attained, but the increase is in a greater ratio than the mere increase of light. This inductive influence upon the gases is not permanent. If they are placed in the dark for a short time, and are afterwards again exposed to the light, an interval of exposure similar to the first is required before the maximum rate of combination is attained.

(880 *b*) The presence of foreign gases in the mixture of chlorine and hydrogen greatly diminishes its sensitiveness to the action of light: thus the addition of 3 parts of hydrogen to 1000 of the

mixture reduced the rate of combination for equal amounts of exposure from 100 to 37·8. The effect of oxygen is still greater; 5 parts of oxygen in 1000 of the mixture reduced its sensitiveness under similar exposure from 100 to 9·7, and 13 parts of oxygen to 2·7. The following table shows the results obtained with these and some other gases,—taking the amount of condensation observed in equal times with the pure mixture of equal measures of chlorine and hydrogen as in all cases equal to 100.

Rate of Combination for Intervals of equal Exposure to Light.

Nature of Foreign Gas.	Vol. of Chlorine and Hydrogen.	Vol. of Foreign Gas.	Ratio of Condensation.
None	1000	0	100
Hydrochloric Acid . .	1000	1·3	100
Chlorine	1000	10	60·2
		75	50·3
		180	41·3
Hydrogen	1000	3	37·8
Oxygen	1000	5	9·7
		13	2·7

Bunsen and Roscoe found that a gas consisting of equal measures of chlorine and hydrogen could be obtained with certainty, by the electrolysis of a solution of hydrochloric acid of sp. gr. 1·148, if a sufficient interval were allowed for the liquid to become saturated with the two gases. This gaseous mixture gave perfectly constant results for equal exposure to a light of uniform intensity, provided care was taken to ensure the complete expulsion of air from the apparatus. The constant source of light which they employed was a jet of coal gas, burned from a platinum nozzle, and connected with a special apparatus for regulating the efflux of the gas. The coloration of the flame by a trace of foreign matter materially affected its chemical activity.

Chlorine and carbonic oxide gas also enter slowly into combination under the influence of sunshine. Two measures of chlorine and two of carbonic oxide thus become condensed into 2 measures; the result is the formation of the irritating pungent gas known as phosgene gas (327), in allusion to the mode of its production. It is remarkable that the direct union of these gases cannot be effected in any other manner.

Organic chemistry abounds with instances in which combinations and decompositions are effected by chlorine, under the influence of the solar ray: a few of these have been mentioned when speaking of the transformations of Dutch liquid (400). The

operation of bleaching linen, by exposure to moisture and light for several weeks during summer, is another process which illustrates the influence of solar light in the production of chemical changes. But the chemical actions produced by the sun's rays, which are taking place unperceived around us, are of infinitely greater importance than those limited transformations which can be effected in the laboratory or the bleach-field; for it is upon these unobserved, yet daily renewed alterations, that the growth and renovation of the entire vegetable kingdom is dependent. The great chemical effect of light appears to be that of a powerful reducing or deoxidizing agent. Under the influence of solar light, the green parts of plants perform their allotted function in the purification of the atmosphere, by absorbing and removing carbonic acid, in virtue of which they fix the carbon in their tissues, and thus supply themselves with food; by a similar decomposition of water they obtain the hydrogen needed for their growth, while they return into the aërial ocean a portion of the oxygen with which the carbon and the hydrogen were previously in combination, and thus assist in maintaining that uniformity in the composition of the atmosphere which is indispensable to the healthful existence of animal life.

If solar light be excluded from plants, none of these decompositions are effected; the carbonic acid escapes unchanged into the air, and no fixation of carbon ensues; the plant becomes pale and succulent, whilst its functions languish. Gardeners take advantage of this knowledge in order to procure vegetables of more delicate flavour; by earthing up the plant, as is practised with celery, or by covering it with a tile as in the case of endive, or by enclosing it in a bell-jar, as is usual with seakale, the light is more or less excluded, and the bleaching which is desired in vegetables for the table is produced.

(881) *Reducing Influence of Light on Metallic Salts.*—Much attention has, within the last few years, been given to the study of the chemical actions produced by light, in consequence of the beautiful inventions of the Talbotype and the Daguerreotype. These remarkable processes, as well as others of a somewhat similar character, appear to depend upon the power which the more refrangible rays of the solar spectrum possess of causing the decomposition of the oxides, chlorides, iodides, or bromides of silver, and of certain compounds of one or two other of the metals. This decomposition by means of light, usually takes place under the concurrent influence of hydrogen, or of some metallic body, which

acts either by setting free the silver or other metal, or by producing a lower oxide, chloride, or other compound of the metal. The alteration of the compound, after its exposure to light, is not always manifested at once by change of colour, but it may be rendered visible by the reactions produced by the application of suitable chemical reagents to the compound after it has been so exposed to the solar ray.

The following instances of the effects of light have long been observed by chemists:—If a piece of white silk be dipped into a solution of chloride of gold, and exposed whilst in a moist state to the sun's light, the silk becomes green, then purple, and in less than an hour a film of metallic gold is produced upon its surface. Nitrate of silver in solution in pure water undergoes no change when exposed to the light, but if any organic matter be added to the liquid, a black deposit is gradually formed; and if the salt be placed upon the surface of the skin, upon paper, or upon linen, the well-known blackening effect for which it is valued as a marking ink for linen is produced. Moist chloride of silver retains its dazzling whiteness if preserved in total darkness, but it assumes a violet tint, which gradually deepens in intensity if exposed even to the diffused light of day,—a portion of chlorine being liberated in the process.

(882) *Photographic Printing.*—The earliest experiments upon the production of pictures by the action of light, appear to have been made by Thos. Wedgwood and Davy in the year 1802. Wedgwood moistened white paper or white leather with a solution of nitrate of silver, and by its means copied paintings on glass, and took profiles; but neither he nor Davy was able to devise any means for preserving these pictures when exposed to diffused light.

The subject attracted but little attention until the commencement of the year 1839, when Fox Talbot made known (*Phil. Mag.* vol. xi.) his process of *photogenic drawing*, which consisted in soaking ordinary writing-paper in a weak solution of common salt, and when dry, washing it over upon one side with a solution of nitrate of silver, consisting of 1 part of a saturated solution of the nitrate with 6 or 8 parts of water. This operation was performed by candle-light, and the paper was dried at the fire; in this manner a film of chloride of silver, mixed with an excess of nitrate of silver, was formed upon the surface of the paper. Suppose that it were desired to obtain a copy of an engraving, or of the leaf of a tree; one of the sheets so prepared was laid under

the engraving or the leaf which was to be copied; the two were pressed firmly together between two plates of glass, and exposed to the direct rays of the sun, or even to diffused daylight, for a period of half an hour or an hour. The impression thus obtained was a *negative* one, that is to say, the shadows were represented by lights, and the lights by shadows; those portions of the surface which had been exposed to the strongest light becoming dark: in the half. tints, where a feebler light had been transmitted, the blackening became less evident; and the parts corresponding to the deep shadows in the engraving remained white. The pictures were fixed by immersing them in a strong solution of common salt. Considerable improvements have been introduced into this process since it was first published, but, in principle, this operation, which has been termed *photographic printing*, remains unchanged.

A very good paper for this kind of printing may be obtained as follows:—Prepare a solution of chloride of sodium or of chloride of ammonium, containing 10 grains of the salt to each ounce of water. If French paper (which is sized with starch) is to be used, it will be improved by dissolving 1 grain of gelatin in each ounce of the solution of salt. Pour this liquid into a flat shallow dish, and having cut the paper into pieces of a convenient size, take a sheet of it by the two opposite corners, and bring it down upon the surface of the solution, so that the middle of the sheet shall be first moistened; then lower it gradually towards each corner so as to exclude air-bubbles. After the lapse of a minute it may be removed from the solution, and hung up to dry. In order to render the paper sensitive, prepare a solution of nitrate of silver containing 50 grains of nitrate to the ounce, and lay the sheet upon the surface of the solution in the same manner as before; in about three minutes' time the sheet may be removed: it must be raised by one corner with a pair of forceps tipped with sealing-wax, allowed to drain, and hung up to dry. The silvering and drying must be performed in a darkened room.

Another sensitive paper, which is often used, may be prepared by forming a solution which contains 80 grains of nitrate of silver in each ounce of distilled water, and adding caustic ammonia until the precipitated oxide of silver is almost redissolved: the solution should be preserved in a dark place. The paper, having been previously salted, is excited by brushing it over with this solution by means of a pledget of cotton wool. The paper is allowed to dry in the dark, and should be used immediately.

In order to protect the picture obtained upon either of these papers from the further action of light, it is now usual to adopt the method introduced by Sir J. Herschel, which consists in soaking the picture in a solution of hyposulphite of soda; this salt combines with the undecomposed salt of silver, and renders it soluble: by washing the picture for two or three hours in water, which should be frequently changed in order to ensure the thorough removal of the salts of silver and of the hyposulphite, the surface is secured from further change when exposed to light.

(883) *Talbotype, or Calotype Process.*—In 1841, Fox Talbot took out a patent for the very beautiful process to which his name has since been attached. In this remarkable operation the surface of the sheet of paper is coated with iodide of silver, which is not sensitive *per se* to the action of light. In order to render it sensitive, it is washed over with a mixture of nitrate of silver with gallic and acetic acids, and then exposed in the camera to the object which is to be copied. After the lapse of a few minutes, (the time required varying with the intensity of the light,) the paper is withdrawn from the camera. Unless the light has been very strong, no image is visible, or a mere outline only, but the compound has undergone a change of a very singular nature, for if the blank sheet be protected from the light and washed over with the mixture of nitrate of silver with gallic and acetic acids, on gently warming it a *negative* image appears with wonderful distinctness and fidelity,—the portions which have been exposed to the strongest lights assuming the darkest tints. The development of the image appears in this process to be due to the reducing agency of the gallic acid, which acts more rapidly upon those portions of the iodide which have been most freely exposed to the action of light. This dormant picture may be developed many hours or even days after it was produced, if the paper be preserved from the light. It seems as though the light, without actually producing a decomposition of the particles of the argentine compound upon which it falls, gives to them a particular condition of unstable equilibrium which predisposes them to decomposition when acted upon by a reducing agent like gallic acid. The process may be conducted in the following manner:—

1. *Preparation of the Iodized Paper.*—A sheet of smooth writing paper, such as that manufactured by Turner, of Chafford Mills, of uniform texture, and free from stains and spots, is pinned upon a board by two of its corners, and brushed over uniformly with a solution of nitrate of silver, containing 33 grains of the

salt in an ounce of distilled water; the sol
means of a brush consisting of a flock of c
through a glass tube, which furnishes a co
the paper is still moist, it is immersed in a
sium, containing 20 grains of the iodide
water, taking care to avoid the occurren
about two minutes, or as soon as the pape
yellow colour throughout, it is transferre
where it is allowed to soak for two or th
water three or four times, so as to remov
each sheet of paper is then to be hung up
to dry. These operations may be condu
in diffused daylight. A stock of this pap
kept for use.

2. *Exciting the Paper for the Camera.*-
camera, prepare 1. a solution of *aceto-nitr*
of 50 grains of nitrate of silver, 1 ounce o
of glacial acetic acid), and 2. an aqueous
saturated in the cold. Add 3 or 4 drops o
to 1 drachm of distilled water, and then in
the mixture freely with a pledget of clear
vered surface of the iodized paper, and w
the superfluous portion with a sheet of c
same sheet of blotting-paper must not
purpose. Whilst still damp it is to be pl
of the camera slide. It will retain its wh
or more.

3. *Exposure in the Camera.*—In order
sheet of the prepared paper is exposed in t
and after a lapse of from five to fifteen or
ing to the amount of light, the picture ma

4. *Development.*—The image is deve
paper over, by means of clean cotton wool,
parts of the solution of aceto-nitrate of
The two solutions must be mixed imme
used, as they speedily undergo mutual de
minutes the picture gradually begins to ap
picture which seems wanting in distinctn
with fresh solution of nitrate of silver. T
be effected by candlelight or in yellow ligh

5. *Fixing the Impression.*—As soon a
acquire distinctness, it is to be well wash
mersed in a saturated solution of hyposu

yellow tint of the iodide of silver has disappeared. It is then to be washed thoroughly for several hours in clean water, frequently renewing the water. Unless all traces of the hyposulphite of silver be removed, the picture will gradually lose its intensity. Fox Talbot originally employed a solution of bromide of potassium for fixing these pictures, but the hyposulphite of soda is to be preferred. When dry, the photograph should be waxed by placing it between two sheets of blotting-paper saturated with white wax, and then passing a moderately heated smoothing iron over the whole. The negative pictures thus obtained may be employed to furnish *positive prints*, or prints with the lights and shadows as they occur in nature, by Talbot's original 'photogenic' process, or by printing upon a second sheet of the prepared Talbotype paper.*

(884) *Photography on Collodion.*—An important modification of Talbot's process was introduced by Mr. Archer, who substituted for the iodized paper a transparent film of iodized collodion spread upon glass, as the recipient of the negative picture. The process is thus rendered more certain and very much more rapid, at the same time the manipulation is simplified, whilst the positive pictures obtained by transference of the negative impression are much sharper in their outline. The operation requires to be conducted in a manner different from that which is practised when paper is employed. The following is the method to be pursued:—

1. *To prepare the bath of nitrate of silver*, take of nitrate of silver 300 grains, dissolve the salt in 2 ounces of distilled water, and add $1\frac{1}{2}$ grain of iodide of potassium dissolved in half a drachm of water, then add drop by drop a solution of carbonate of potash till a slight permanent turbidity is produced; afterwards add distilled water until the mixture measures 10 ounces; filter, and add $2\frac{1}{2}$ minims of glacial acetic acid.†

2. *Preparation of Solution of Collodion.*—A solution of iodized collodion, which is suitable for the formation of negative pictures, may be prepared as follows (Hardwich):—Take of rectified ether (sp. gr. 0·725), and of alcohol (sp. gr. from 0·805 to 0·815),

* For further details upon the subject of photographic printing, &c., the reader is referred to Hardwich's *Manual of Photographic Chemistry*.

† Ordinary nitrate of silver is apt to contain a trace of nitric acid, which it is desirable to neutralize, as an acid solution is much less sensitive to the action of light than a neutral one. It is still more important, however, not to have any alkaline reaction, and as carbonate of silver is slightly soluble in the nitrate, the addition of acetic acid is subsequently made, to guard against this: the iodide of potassium is added in order to saturate the bath with iodide of silver; if this precaution were not taken, the film of iodized collodion would be liable to lose a portion of iodide of silver, since this salt is also somewhat soluble in a solution of nitrate of silver.

each 4 fluid drachms; soluble pyroxylin,* from 4 to 6 grains; iodide of potassium or ammonium, 2 grains; iodide of cadmium, 2 grains. First dissolve the iodides in the alcohol, then add the pyroxylin, and lastly the ether. Agitate the materials well, set them aside for twenty-four hours, and then decant the clear liquid, which will retain sufficient sensitiveness to admit of being used even at the end of a month after its preparation.

3. *Preparation of the Collodion Film.*—In order to make use of this solution, a plate of glass cut to the size required for the camera (after being washed with a solution of potash to free it from grease, rinsed in water, dried, and wiped with a clean silk handkerchief), is to be held horizontally in the left hand, and a portion of the collodion is to be poured steadily on the middle of the glass, and by slightly inclining the plate in different directions, made to flow completely over the upper surface; the excess of the solution is immediately to be poured back into the bottle.

4. *Exciting the Plate for the Camera.*—The nitrate bath having been introduced into a trough of glass or of gutta percha sufficiently wide to allow the introduction of the glass plate upon which the collodion is spread,—the prepared plate, within half a minute after the film has been poured off its surface, is introduced into the solution of nitrate of silver; in from two to three minutes' time it is thoroughly impregnated with iodide of silver, and when withdrawn from the bath it has assumed a cream-coloured opalescence. These operations must be effected in a room illuminated by light admitted through a yellow blind, or by the light of a candle screened by yellow glass (890).

5. *Exposure in the Camera.*—The prepared plate is to be immediately introduced into the slide of the camera, in which it is to be exposed to the object for a few seconds (from 3 or 4 to 30 or 40), according to the nature of the object and the intensity of the light. The slide is then withdrawn from the camera,

* A suitable pyroxylin for this purpose may be obtained in the following manner:—Take of oil of vitriol, sp. gr. 1·843, six fluid ounces; pure nitrate of potash, finely-powdered and dried, 3½ ounces avoirdupois; water, 1 fluid ounce; dried cotton wool, 60 grains. Mix the acid and water, and add the nitre, gradually stirring between each addition, until the whole of the salt is dissolved. Suffer the mixture to cool to 150° or 145° F., then add the cotton wool in small tufts at a time, taking care to plunge the cotton completely beneath the surface; cover it, and allow it to stand for ten minutes. Then press out the acid with a glass rod as completely as possible, and throw the pyroxylin into a large volume of cold water, and wash for half an hour; afterwards soak it well in water for some hours; lastly, wring it out in a cloth, and dry at a heat not exceeding 100° F. The substance thus obtained is completely soluble in a mixture of ether and alcohol. It is essential to attend to the strength of the acid and to the temperature employed.

and the plate when examined will not be found to exhibit any image.

6. *Developing the Image.*—A latent image, however, exists, and it may be developed by the use of a liquid prepared by dissolving 1 grain of pyrogallic acid, from 10 to 20 minims of glacial acetic acid, and 10 minims of alcohol, in an ounce of distilled water. Half an ounce or more of this liquid is to be poured over the plate immediately after its removal from the camera. The negative image which is thus gradually developed, will be more intense if immediately before using the pyrogallic solution an addition be made to it of the same solution of nitrate of silver as is employed in the bath, in the proportion of 2 drops to each drachm of the developing liquid.

The exact reaction which occurs in this remarkable process is not known. The pyrogallic acid, however, is a substance which has a strong tendency to combine with oxygen; and under the conjoined action of iodide of silver and nitrate of silver (the presence of the latter salt in excess being necessary to the reaction) a portion of silver is reduced, perhaps in the manner represented by the subjoined symbols, in which P represents pyrogallic acid :—

$$(1)\quad \overbrace{Ag\,I}\quad \overbrace{AgNO_6}P, \qquad (2)\quad Ag\quad \overbrace{IAg}\quad \overbrace{NO_6P}$$

Unless the plate has been exposed to light, the result would be such as is shown in No. 1, in which no action is represented as having occurred. In No. 2 the silver is represented as having been liberated upon the surface of the film of collodion, the quantity of iodide of silver remaining unaltered, but the iodine being transferred to a particle of silver previously in combination with nitric acid, whilst the nitric and pyrogallic acids react upon and decompose each other.

Other solutions may be employed for developing the latent image. One which answers very well for this purpose consists of, —crystallized sulphate of iron from 12 to 20 grains, glacial acetic acid 20 minims, alcohol 10 minims, and water 1 ounce. It is not, however, so well adapted for the production of intense negatives as the pyrogallic acid. When the picture is sufficiently distinct, it must be washed with clean water, and fixed by immersing it in a solution of hyposulphite of soda (1 part of the salt to 2 of water) till the cream-coloured iodide of silver is entirely removed. A solution of cyanide of potassium, containing from 2 to 12 grains of the salt in an ounce of water, may be substituted for the hyposulphite of soda for the purpose of fixing the image. The picture

is again to be thoroughly washed in clean water; it is allowed to dry, then heated before a fire until it feels slightly warm, and the film is protected from mechanical injury by covering it with a coat of transparent spirit-varnish by a manipulation similar to that employed in coating the plate with collodion. This varnished photograph may then be employed for procuring positive pictures by means of the sensitive paper prepared with chloride of silver upon Fox Talbot's plan (882). By rendering the collodion perfectly neutral, the sensitiveness of the film to the action of light may be so highly exalted, that moving objects, such as the waves of the sea, or a crowd of people, may be successfully depicted by the instantaneous action of light upon the plate.

(885) *Albuminized Plates.*—Niepce de St. Victor introduced the employment of glasses coated with albumen, prepared by beating up whites of eggs with 1 per cent. of iodide of potassium: the liquid is to be placed for 12 or 24 hours in deep vessels, to become clear, after which the supernatant liquid is to be poured upon glass so as to produce a uniform layer; it is then allowed to dry for 12 hours, and is fit for the bath of nitrate of silver. Albuminized glasses may be preserved for some weeks without injury; they may be excited by means of Talbot's mixture of aceto-nitrate of silver with gallic acid (883). The image is developed by means of a solution of gallic acid, after the plate has been exposed in the camera.

(886) *Photographic Engraving and Lithography.*—In the year 1827, Niepce published a process for obtaining pictures by the aid of light, the basis of which was the fact that the bitumen of Judæa, when exposed to the sun's rays, becomes insoluble in oil of lavender, whilst those parts which have remained in shadow preserve their solubility. This process has, with some modification, been applied by Niepce de St. Victor, the nephew of the inventor, to the production of engravings upon steel. Powdered asphalt and a proportion of pure beeswax are dissolved in oil of lavender, and then mixed with an equal volume of benzol. The surface of the steel plate which is to be engraved is first carefully cleaned with whiting and water, after which a solution of hydrochloric acid in 20 parts of water is poured over it, and the plate is immediately washed and dried. The solution of bitumen is then poured upon the plate in a darkened chamber, and dried by the application of a gentle heat. A good *positive* photographic proof is now applied to the surface, covered with glass, and exposed for a short time to the action of diffused light. The exposed plate is next subjected to the action of a mixture of 3 parts of rectified naphtha and 1 of

benzol; the parts which have not been exposed to light are gradually acted upon by this mixture. When the process of solution has proceeded far enough, the solvent is washed off with water, and the exposed parts of the plate are 'bitten in' with a mixture of 1 measure of nitric acid, sp. gr. 1·33, 2 measures of alcohol, sp. gr. 0·844, and 8 measures of water. The plate is then submitted to the ordinary processes employed in aquatint engraving.

An important modification of a process proposed by Poitevin for producing lithographs by the aid of photography, has been introduced by Mr. Osborne of Melbourne. The basis of this operation is the observation that a mixture of bichromate of potash and gelatin when exposed to light becomes insoluble in water. In order to apply this to practice, Mr. Osborne coats a sheet of smooth paper with albumen, and subjects it to pressure against a surface of polished metal; he afterwards coats it with a solution of bichromate of potash in gelatin, and again subjects it to pressure. These operations are conducted in a room illuminated by yellow light. Paper thus prepared may be preserved unaltered for a long time if excluded from light. In order to use it, a negative picture prepared in the usual way is placed over one of these sheets of chromate paper, and exposed for a few minutes to a good light, with the precautions usual in photographic printing. Owing to the partial reduction of the chromic acid in the parts exposed to light, a positive picture will now be obtained, the parts acted on by light becoming brown, whilst the screened portions retain their original yellow colour. When the picture thus produced is placed in water, the unchanged portions are easily washed away, leaving the altered portions attached to the paper. In practice, it is found best to cover the whole surface of the picture with a coating of lithographic ink, and then float the back of the paper upon boiling water. After soaking for a short time the surface may be sponged, and the screened portion may be completely removed, leaving a beautifully defined positive impression of the negative picture. After washing it with boiling water, the design is, by means of pressure, transferred to the lithographic stone, and the prints, which may be obtained from this transfer in the usual way, are remarkable for their sharpness and delicacy.

Very nearly at the same time as Mr. Osborne, Sir H. James made an independent application of the bichromate process of Asser of Amsterdam to zincography. The liquid which he uses consists of a mixture of 2 measures of a solution of bichromate of potash (saturated at the boiling point) with 1 measure of a solution of 3 parts of gum arabic in 4 of water, and the transfer is

made to a plate of zinc instead of to the lithographic stone. He has applied the process successfully to the copying of old engravings and manuscripts, as well as to the multiplication of maps and plans.

(887) *Chrysotype*.—Other processes more or less analogous to the Talbotype have been contrived: one of them was invented by Herschel, and described by him under the name of the *chrysotype* (*Phil. Trans.*, 1842, pp. 206, 209):—Paper is washed over evenly with a solution of ammonio-citrate of iron, of such a strength as when dry to produce a good yellow colour. It is placed in sunshine in a camera, or under any engraving which it may be intended to copy; after a few minutes' exposure it is to be removed, and instantly washed over with a neutral solution of chloride of gold; a positive picture is thus developed, which assumes great sharpness, becoming gradually deeper up to a certain point; at the instant when it ceases to gain in intensity (this point being easily seized by practice), the picture is put into pure water, and rinsed thoroughly in order to remove the excess of solution of gold; it is then fixed with a solution of iodide of potassium, and again washed to remove the superfluous salts.

In this case the persalt of iron, under the influence of the organic matter of the paper, becomes partially reduced to a salt of the protoxide, in the parts exposed to light; and this protosalt of iron, when washed over with the solution of gold, precipitates the latter metal in the reduced state, and thus gives rise to the coloured image. Water, by removing the excess of the salts, fixes the picture and prevents it from experiencing further change on exposure to light.

If ferridcyanide of potassium be employed instead of chloride of gold, for developing the picture, a blue image will be produced, owing to the formation of Turnbull's blue, upon the reduced portions of the salt of iron.

A solution of pernitrate of uranium may be used instead of the ammonio-citrate of iron, and the picture may be developed by means of a solution of nitrate of silver, of chloride of gold, or of the salt of some other easily reducible metal.

(888) *Daguerreotype*.—In the year 1839, Daguerre made known his beautiful method of obtaining photographic pictures upon metallic plates. The essential parts of this process are as follows:—A sensitive film of the iodide of silver upon a silver plate is exposed to the action of light in the camera. The latent image is then developed by exposure to the vapour of mercury, after which the picture is fixed by means of hyposulphite of soda.

1. *Polishing the Plate.*—For this purpose a polished sheet of plated copper is taken, and cleaned by rubbing it over first with finely powdered tripoli on a pledget of cotton moistened with a few drops of alcohol, and afterwards with dry cotton, until, when breathed upon, the metal assumes a uniform dull surface, from which the cloud disappears without showing any patches or spots; after this the plate is carefully polished, by means of a long polishing board faced with buckskin. If this preliminary operation be not carefully performed, the subsequent steps will not lead to any satisfactory result; the touch of a finger upon the polished surface is sufficient to soil it.

2. *Iodizing.*—The plate is next exposed for a few minutes to the vapour of iodine, till a thin yellow film is produced uniformly over the surface. This operation should be performed by candle-light, or in a room furnished with a window supplied with yellow glass; the plate must be protected from diffused daylight.

3. *Exposure.*—If such a plate be exposed for a few minutes in the focus of a double achromatic lens, adjusted to a camera obscura in such a manner that the image of the object to be copied shall fall upon the iodized surface, it undergoes an alteration which, however, is not perceptible on withdrawing the plate from the camera.

4. *Development.*—But if the plate be exposed for a few minutes to the vapour of mercury, heated to about 140° F., the latent image gradually appears, with all the shadows, lights, and half-tints faithfully reproduced. Much of the success depends upon the proper length of exposure to the action of light, and in this respect practice is the best guide; if too short a time be allowed, the picture is dark and indistinct; if the light has acted too powerfully, the shadows become metallic in appearance, and ill-defined; and if the action be continued for a sufficient length of time, the picture becomes reversed, or *negative,* the shadows in such a case being represented by lights, and the lights by shadows. A due exposure to the mercurial vapours constitutes an important part of the operation; for if this exposure be insufficient, the whites have a bluish cast, and if it be too long continued, the blacks become indistinct and misty.

Mr. Goddard, in the year 1841, discovered that the iodized plate may be rendered very much more sensitive to the action of light, by exposing it for a few seconds to the vapour of bromine, or of chloride of bromine, so as to obtain a mixed film of iodide and bromide of silver, or of iodide, chloride, and bromide of silver. The process thus was rendered applicable to portraits, and the

operation could be accomplished in as many seconds as it before required minutes. The usual practice now is, after having obtained an orange-coloured film by exposure of the silver plate to the vapour of iodine, to expose it to the fumes of bromine from bromide of lime, until the film assumes a rose colour; after which it is a second time returned to the iodine box for a period equal to one-third of that occupied by the first iodizing. The plate is then exposed in the camera, after which it is mercurialized.

In order to fix these pictures, Daguerre employed a solution of hyposulphite of soda, and then washed the plates with water. The effect of the Daguerreotype may be much improved by gilding them by the process of Fizeau; they are thus rendered less liable to mechanical injury, and a richer and a warmer effect is given to the impression:—for this purpose, 1 part of neutral chloride of gold and 3 parts of hyposulphite of soda may be dissolved in 500 parts of water; the plate having been placed in a horizontal position, is to be completely covered with a small quantity of this liquid, and the plate is heated by a large spirit-lamp flame until small bubbles appear on its surface. A thin film of reduced gold is thrown down all over the picture, and by this operation the shadows are deepened and the lights rendered more brilliant. It must then be washed with distilled water, drained, and dried by the application of a gentle heat to the back of the plate.

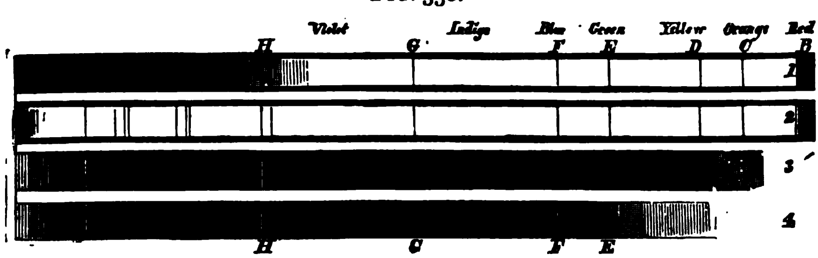
The following theory may be offered in explanation of the changes which occur during the production of the Daguerreotype image:—Under the influence of light the superficial layer of iodide of silver is modified so as to render it susceptible of decomposition. When the plate is acted upon by the mercurial vapour, the iodine is driven to the deeper layer of silver, and a film of silver is liberated upon the surface of those parts which have been exposed to the action of light, the thickness of this film varying with the intensity and duration of the light. The reduced silver combines with the mercury, and a film of silver amalgam is formed, which varies in thickness with the thickness of the silver film, in consequence of which the reflected tints differ according to the varying thickness of this film: those parts of the iodized plate which have not been exposed to the light, of course do not combine with the mercury. After the plate has been treated with hyposulphite of soda, the excess of iodide of silver is removed, and the blacks consist of metallic silver. Experiment proves that those parts of the plate immediately beneath the highest lights are more deeply corroded than the others by the action of the iodine, which has been driven inwards during the process of mercurialization.

In complete accordance with the foregoing explanation, is a curious fact first pointed out by Mr. Shaw, that if a plate after it has received the impression in the camera, but before it has been mercurialized, be exposed to the vapour of iodine or of bromine for a few seconds, the image is completely effaced, and is no longer producible by mercury.

The surface of the plate is rendered uneven by the combined operation of light and mercury upon it, so that it admits of being copied by the process of electrotyping (874). Impressions on paper have been printed from an etched Daguerreotype plate, the biting-in being produced by diluted nitric acid, which attacks the shadows (the reduced silver), and leaves the lights (the amalgam) untouched.

(889) *Action of the Solar Spectrum on Photographic Bodies.*—If a pure solar spectrum be allowed to fall upon a sheet of sensitive paper, prepared by washing it over first with common salt, and then with nitrate of silver, it will be speedily apparent that the chemical action is not uniformly distributed over the luminous image. The maximum of light falls in the yellow rays about

FIG. 350.

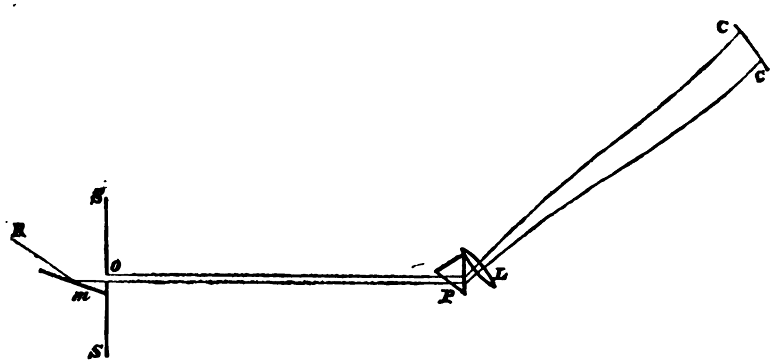


Fraunhofer's line D (fig. 350), whilst the maximum of chemical action occurs in the blue portion of the spectrum, near the line G, about one third of the distance between it and the line H. The blackening effect generally extends as far as F in the green, whilst it is prolonged beyond the violet end of the spectrum to a distance nearly equal to two thirds of the length of the luminous spectrum, the chemical effect gradually shading off until it becomes imperceptible; the maximum point of action, however, varies with the preparation which is used. When the Talbotype iodized paper is employed, the maximum blackening is found on the extreme limit of the violet rays. Where the bromide of silver forms the sensitive material, the chemical action is prolonged into the red ray, and the greater part of the impression is of a uniform grey black. When paper washed with chloride of gold is employed as the sen-

sitive surface, the maximum effect is produced between the green and the blue rays, and the chemical action does not extend beyond the violet extremity for more than half the distance over which these effects are produced upon the salts of silver. In fig. 350, 1 represents the space occupied by the luminous spectrum on white paper; 2, the same spectrum thrown on a fluorescent screen, viz., turmeric paper,—by which it is rendered visible almost to the extreme limit of chemical action; 3, the chemical spectrum on bromide of silver; 4, the Talbotype spectrum. Herschel, Hunt, and E. Becquerel have each succeeded more or less perfectly in obtaining coloured impressions of the spectrum upon chloride of silver, but they have been unable to fix them. Herschel (*Phil. Trans.*, 1840) says that the impression "was found to be coloured with sombre but unequivocal tints, imitating those of the spectrum itself." The coloration commenced in the orange rays. Becquerel appears to have obtained more brilliant colours by employing a plate of silver which had been superficially converted into subchloride by immersing it in diluted hydrochloric acid, and then making it the positive plate of a voltaic battery.

Inactive spaces occur in the chemical spectrum, which correspond exactly with those which are found in the visible spectrum, but they extend also into the prolongation beyond the violet extremity, and occur there in great number. These fixed lines may be obtained upon Talbotype paper, or, still better, upon a surface of collodion, in the following manner:—

FIG. 351.



Let S S (fig. 351), represent a shutter of a room which can be rendered completely dark; O is an opening or slit of about $\frac{1}{40}$th of an inch wide, through which a beam of solar light is reflected by a heliostat *m*, or from a mirror, the angle of which to the ray admits of

regulation from within the room; L is a lens of from 20 to 30 inches focal length; P, a prism;—the lens and prism may be made of glass free from striæ, but they are best constructed of rock crystal: the distance of L from the aperture is equal to twice its focal length. If the prism be placed so as to produce the minimum deviation of the ray, and as close to the lens as can be,—at C C, which is at as great a distance behind the lens L as O is in front of it,—a spectral image of the aperture will be formed, and may be received upon a screen. All the coarser lines of the visible spectrum may be traced by the unaided eye, when the spectrum is received on a screen of white paper: and if a sheet of turmeric paper be used, many of the lines beyond the violet are also rendered visible: by substituting a sensitive surface, such as collodion, for the screen of white paper, a faithful copy of these lines may be obtained.

It is remarkable that the chemical rays appear to be identical with those which produce fluorescence (104). If the solar rays be transmitted through a layer of a concentrated but colourless solution of sulphate of quinine, no extra-spectral prolongation of chemical action is produced when this light is allowed to fall upon a sensitive surface. By varying the source of light, the chemical powers of the spectrum are varied also. The chemical action of the flame of the hydrocarbons, however intense the light, is but feeble; that of the lime light is much more marked, while that of the electric light between charcoal points greatly surpasses either; and these results coincide exactly with their relative power of exciting the phenomena of fluorescence.

Bunsen and Roscoe (*Phil. Trans.*, 1857, 601) have made experiments upon the absorbent power of chlorine upon the chemical rays which affect the combination of a mixture of chlorine and hydrogen. They find that when light passes through a medium in which it excites chemical action, a quantity of light is absorbed proportional to the chemical effect produced. Thus the chemical power of the light of a coal-gas flame of a certain intensity measured by its activity in producing the combination of chlorine with hydrogen was found to be reduced to $\frac{1}{10}$th when transmitted through a column of chlorine 6·822 inches in depth; if the chlorine were diluted with an equal volume of air, the length of the column required to produce a similar absorption was exactly double, or 13·644 inches. But when a mixture of equal volumes of chlorine and hydrogen was used, the depth of the mixture which was required to reduce the chemical effect of the light to $\frac{1}{10}$th of its original intensity was only 9·212 inches: thus it appears that a certain quantity

of the active rays are absorbed during the chemical effect.

With light from different sources ana tained, but the amount absorbed was found of the light. Thus the diffused zenith lig the morning was reduced to $\frac{1}{10}$th of its in through 1·794 inches of chlorine, and throug ture of chlorine and hydrogen; the absorben the chemical rays of diffused daylight beir than upon those of coal gas. Observati light showed that a depth of 0·776 inches c to reduce the chemical power to $\frac{1}{10}$th of tl cident light. The relative thickness of t required to reduce the chemical power was therefore the following:—

A flame of coal gas	. . . .
Reflected zenith light (morning)	. . .
Reflected zenith light (evening)	. . .

(890) It was stated more than 50 year observation has been confirmed and extend two ends of the spectrum produce opposite the violet extremity appears greatly to pre for example, paper soaked in nitrate of silv by exposure to diffused daylight, and then of the solar spectrum, the portion upon w speedily becomes much darker, while the rays assumes a brick-red hue. If the sp white paper coated with nitrate of silver, allowed at the same time to fall upon it, rays fall retains its whiteness, while the re darkens. It thus appears, that by com two rays of different refrangibilities, effec cannot be obtained by either ray separatel

Blackened nitrate paper, if washed over of potassium, becomes gradually bleached w daylight. If the solar spectrum be allo thus prepared, whilst moist, and before it h part beneath the violet end is quickly ble bounded by a sharp border in the yellow, the red end becomes darker. The phenon also exhibit similar opposition in the effects extremities of the spectrum (106).

Claudet (*Phil. Trans.*, 1847) found that an iodized Daguerreotype plate, when submitted in the focus of a camera to the red image of the sun as seen through a London fog, became subsequently whitened on exposure to the vapour of mercury, in all parts, except in the track traversed by the image of the sun,—this portion continued perfectly black. In another experiment, a plate was covered with black lace, and exposed to diffused daylight; after a few minutes' exposure, one half of the plate was covered with an opaque screen, the other half with a red glass, and the exposure was continued for a short time: in the mercury box the red half continued black, whilst, on the other portion, the image of the lace was distinctly traced. The photographic effect at first produced over the whole plate had in fact been neutralized by the red glass.* A pleasing variation of the last experiment was made by exposing an iodized plate to diffused daylight, then covering it with a piece of black lace, and screening it with a red glass; a negative picture was now developed in the mercury box, the red glass having destroyed all photographic action except on those parts screened by the lace. Orange and yellow glasses give similar results. After exposing a plate to daylight, and then submitting it to the action of red glass, it again becomes sensitive to light, so that, as Claudet observes, it is no longer needful to prepare the plates in a dark chamber, since, if placed beneath a covering of red glass, they are always ready for immediate use,—even though subsequently to their preparation they may have been for some time exposed to solar light.

But though the red and yellow glass have the power of completely counteracting the effect of the radiation of the more refrangible rays, they have a peculiar effect of their own. The neutralizing power of the red ray is exerted more slowly than the photographic effect of the white light, nearly in the proportion of 100 to 1; that of the yellow ray was found to be about 10 to 1.

From the foregoing remarks, it is evident that the colour of objects must exert a material influence upon the nature of the photographic images produced. Reds and yellows, from the want of chemical energy in the less refrangible portion of the spectrum, will be characterized by absence of photographic action in the

* It must be borne in mind that all results obtained by coloured media are liable to ambiguity, for it seldom happens that the light transmitted through them is homogeneous (102); the effects are liable to become complicated from the intermixture of results produced by rays from different parts of the spectrum.

image, and will be represented by black spots, which often produce singular disfigurement in portraits. Yellow freckles, for instance on the skin of the face are accurately copied, but are depicted in the portrait as black spots. Much judgment and knowledge are therefore required in selecting a dress of a colour which is adapted to produce a suitable depth and contrast of tint in the photograph.

(891) *Action of the Solar Spectrum on Vegetable Colours.*—This subject has been particularly examined by Herschel (*Phil. Trans.*, 1842). White paper coloured with various vegetable juices was subjected by him to the influence of the prismatic spectrum, and in some cases these papers were washed over with solutions of metallic salts. The following are the most important general conclusions which may be drawn from these experiments:—1. That the action of light is in almost all cases of a nature to obliterate the colour; or if it does not entirely bleach it, a faint residual tint is left, upon which it has little further action. The older the paper or the tincture, the more decided is this residual tint, which is probably the result of an oxidizing action upon the colouring material, independent of the action of light. 2. The action is confined to *luminous* rays of the spectrum,—offering in this respect a marked difference between these actions and those produced upon the metallic compounds. 3. The rays which are most effective in destroying a given tint are in many cases those which are complementary (102) to the tint destroyed. Orange-yellows, for instance, are bleached most powerfully by the blue rays: blues by the red, orange, and yellow rays; and purples and pinks by the yellow and green rays.

CHAPTER XIX.

ON THE DETERMINATION OF THE COMBINING NUMBERS OR ATOMIC WEIGHTS OF THE ELEMENTARY BODIES.

(892) *Aid derived from Analysis in fixing the Combining Number of a Body.*—The determination of the combining number of a body is an operation of great delicacy, and often involves many very difficult questions. The first object of the chemist is to select some compound of the elementary body under examination, the composition of which is tolerably simple, and which can readily

be procured in a state of purity, and in this compound he determines the proportions of each of its components with the utmost attainable precision. It is of great importance that the operations by which these results are obtained should be as few in number, and as simple and manageable as possible. It is not, however, sufficient that three or four different experiments conducted in the same manner should give uniform results: the mode of analysis adopted should, if possible, be varied so as to avoid any unperceived source of error which depends upon the process employed. It is also desirable to vary the compound upon which the analysis is made. Thus, the equivalent of a metal may in some instances be ascertained by fixing the proportion of oxygen which a given weight of the metal requires for its conversion into the state of oxide: in other cases the proportion of oxygen and of metal can be determined very exactly by ascertaining the loss of weight which the oxide experiences when a known weight of the pure oxide is heated in a current of hydrogen. It is, however, advisable to check these results, not only by trials upon different quantities of the metal or of the oxide prepared at different times, but also (in order to guard against the occurrence of any unperceived impurity in the substance under experiment) to ascertain if the analysis of the chloride, the sulphide, or some other compound of the metal, gives a similar numerical value for its combining proportion. These results must be reduced, by calculation, to their weight *in vacuo* (23).*

(893) *Aid derived from Isomorphism, Specific Heat, and Combining Volume of Vapour.*—The determination of the numbers which are assumed to represent the relative atomic weights of the elements, however, does not rest simply upon the knowledge of the proportion in which each element enters into combination with a given amount of oxygen or of any other simple body. When a substance forms but a single combination with oxygen, the simplest hypothesis respecting its composition is that the compound so formed is produced by the union of single atoms of each of its components. Thus magnesium and zinc each forms but a single oxide, and they are assumed to be protoxides,—or oxides, each compound atom of which contains 1 atom of the metal to 1 atom of oxygen. Such oxides neutralize a quantity of nitric acid which contains five times as much oxygen as the base. But it not unfrequently happens that the same metal forms two oxides, in one of

* Some idea of the extraordinary care required in researches of this description may be formed by the perusal of the admirable memoir of Stas, in the Transactions of the Brussels Academy for 1860.

which a given weight of oxygen combines with twice as large a proportion of the metal as in the other: for example, 8 parts of oxygen unite with either 31·75 of copper to form the black oxide, or with 63·5 of the metal to form the red oxide, and both oxides can combine with acids. In like manner, 8 parts of oxygen form with mercury two salifiable oxides, one containing 100, the other 200 parts of mercury. The question to be determined then is, which of these numbers is to be regarded as representing the atomic weight or equivalent of the metal? In cases of this kind, the judgment requires aid from analogy, or from collateral circumstances, such as the isomorphism of the body with some other analogous compound of known composition; the circumstance that the specific heat of the body, when multiplied into its supposed atomic weight, yields the same product as that obtained by multiplying the specific heat of some other element into its admitted atomic number; or the formation of a volume of vapour from the supposed equivalent which is equal in bulk to the volume of an equivalent of hydrogen.

Such assistance is afforded in the case of copper by the isomorphism of the compounds of the black oxide of this metal with corresponding compounds of zinc and magnesium. If the oxide of zinc be a protoxide, the black oxide of copper is also a protoxide, and the red oxide must be considered as a suboxide.

Another character of some importance, but subordinate to that of isomorphism, is afforded by the specific heat of the metal. Assuming the oxide of zinc to be a protoxide, the atomic number of the metal is 32·7, and its specific heat is found to be 0·0955; the product of these two numbers is 3·103. The specific heat of copper is 0·0951, and assuming the black oxide to be the protoxide, the atomic weight of the metal is 31·75; the product of these two numbers is 3·019, or nearly the same as in the case of zinc; whereas, if the red oxide were assumed to be the protoxide, it would be double this number.*

In the determination of the atomic weight of mercury, assistance may be derived from another character of much higher importance; since as it is a volatile metal it can be converted into vapour, and the density of that vapour can be ascertained. Now

* If, however, this consideration were allowed to be decisive, it would be necessary to modify the numbers generally received for several of the elements. The numbers assigned in the table to bromine, to iodine, to phosphorus, to arsenic, to antimony, to bismuth, to potassium, to sodium, to silver, and to gold, would require to be reduced by one half, and in many cases, as in that of the halogens, this procedure would be objected to on chemical grounds.

the specific gravity of the vapour of mercury is 6·974, and that of hydrogen is 0·0692; or, allowing for unavoidable errors of experiment, the density of mercurial vapour is 100 times as great as that of hydrogen. If the atom of hydrogen = 1 it gives a volume of vapour which occupies double the space of that required by an equivalent of oxygen. If 100 be assumed as the atomic weight of mercury, it yields a volume of vapour equal to that of an equivalent of hydrogen, or double that of oxygen, thus corresponding with nitrogen and the halogens; whereas, if 200 be the atomic weight of mercury, 1 atom would yield 4 times the volume of vapour afforded by an equivalent of oxygen, which would be highly improbable, since no other element possesses a similar vapour volume. There are, however, several anomalies in vapour volume which render even this character in some cases ambiguous. These difficulties will be more particularly adverted to hereafter (1466).

It is not safe, moreover, to assume in cases in which only one compound exists between an element and oxygen, that such compound is necessarily a protoxide; aluminum is not known to form more than a single oxide, yet chemists do not hesitate to consider this oxide as a sesquioxide, and in this judgment they are guided by analogy:—Thus, those bodies which are admitted to be protoxides are generally powerful bases, and neutralize the acids very completely. Now alumina does not present this character; its salts have a powerfully acid reaction and taste. But the arguments of most weight against the supposition that alumina is a protoxide, are derived from the composition and properties of the oxides of iron. Iron forms two basic oxides: one contains but two thirds of the proportion of oxygen which is present in the other. The oxide of iron with the smaller proportion of oxygen is a powerful base, and with acids forms salts which are isomorphous with those of magnesia and oxide of zinc. It is consequently regarded as a protoxide, and the other oxide is looked upon as a sesquioxide; the basic properties of the latter are much more feeble, and the salts which it forms with acids have, like the salts of alumina, a powerfully acid reaction. Sesquioxide of iron, moreover, is isomorphous with alumina when in combination. An iron alum may be obtained in octohedral crystals, in which the place of the aluminum is supplied by that of iron: and native peroxide of iron is found in forms of the rhombohedral system isomorphous with native alumina in corundum. Hence, if the red oxide of iron be a sesquioxide, alumina must be a sesquioxide also.

An excellent illustration of the value of isomorphism in these cases is also afforded by the oxides of chromium. Until the pub-

lication of Péligot's researches on this metal, only two compounds of chromium with oxygen were known, viz., the green oxide, and chromic acid,—the acid containing twice as much oxygen as the oxide. In these two compounds the proportion of oxygen combined with the equal weights of chromium was as 1 : 2, or as $1\frac{1}{2}:3$. But there was little difficulty in deciding that the green oxide must be regarded as a sesquioxide, for the green oxide of chromium was known to be isomorphous with the red oxide of iron, both in its uncombined form, and when in combination with the same acids. Chromic acid would, therefore, contain 3 atoms of oxygen to 1 atom of the metal. But evidence still more conclusive of the accuracy of this view is afforded by the fact that chromic acid is isomorphous with manganic acid; the latter is known to contain 3 atoms of oxygen, for it is the acid of a metal which yields an oxide with a given weight of manganese containing one third of the oxygen present in manganic acid, and which moreover is isomorphous with the protoxide of iron. Finally, the discovery of another oxide of chromium, with a smaller proportion of oxygen than either of the compounds previously known, fully vindicated the correctness of the foregoing deductions; for the new oxide was found to contain one third of the proportion of oxygen present in chromic acid. It also yielded salts isomorphous with the corresponding salts of the protoxide of iron, and the proportion of oxygen which it contained bore the same relation to that present in the green oxide of chromium that the oxide in the protoxide of iron did to that in the red oxide of iron. Péligot's new oxide therefore was the missing protoxide of chromium.

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(894) *Numerical Data from which the Equivalents or Atomic Weights of the Elements have been calculated.*

The atomic weights of the elementary substances were first investigated with precision by Berzelius, and the numbers obtained by him, with certain important corrections, are those at present in use. These researches of Berzelius, combined with those of subsequent chemists, particularly of Dumas (*Ann. de Chimie,* III. i. 5; viii. 189; and lv. 129); of Pelouze (*Comptes Rendus,* xx. 1047); of De Marignac (*Bibliothèque Univ. de Genève,* xlvi); of Erdmann and Marchand (*Journal für prakt. Chemie,* xxiii., xxvi., xxxi., and xxxiii); and of Stas (*Trans. Brussels Academy,* 1860), have furnished the following data, from which the numbers given at p. 18, Part I. have been compiled:—

1. *Aluminum.*—Berzelius found that 100 parts of the tersulphate of alumina ($Al_2O_3,3\,SO_3$) lost by intense ignition 70·066 of sulphuric acid; hence assuming the atomic weight of sulphuric acid as 40, that of aluminum (hydrogen being = 1) is 13·672. Dumas, by determining the amount of silver required to precipitate a given weight of chloride of aluminum, concluded, from a mean of seven experiments, that the atomic weight of aluminum is 13·744; or if oxygen be 100, it is 171·8.

2. *Antimony.*—The number 129·03, assigned by Berzelius to antimony, is admitted to have been too high. Schneider, by reducing the native sulphide to the metallic form, obtained on the average 71·469 per cent. of metal, which would yield as the combining number 120·3. The experiments of Rose on the chloride gave 120·69. Dexter, by oxidizing the metal with nitric acid, and converting the residue by ignition into Sb_2O_3, obtained 122·34 as a mean result; and Dumas by experiments upon the terchloride found the quantity of silver required to precipitate the chloride indicated 122·0, or 1525 as the combining number of the metal.

3. *Arsenic.*—Pelouze decomposed a given weight of chloride of arsenic by means of water, and determined the quantity of chloride of silver which it produced: a mean of three experiments gave 75, or 937·5 as the atomic weight of arsenic, a result confirmed by four experiments of Dumas, which gave it as 74·95.

4. *Barium.*—Berzelius found that 100 parts of chloride of barium when dissolved in water yielded 112·175 of sulphate of baryta, on the addition of sulphuric acid; and that 100 parts of the chloride when mixed with a solution of nitrate of silver yielded 138·07 of chloride of silver. Pelouze, by precipitation with silver, obtained results almost identical: the number given by Berzelius for barium is 68·42; that by Pelouze is 68·64. De Marignac, from a series of experiments of the same kind, checked by the determination of the baryta as sulphate, adopts the number 68·58; and Dumas, as a mean upon sixteen experiments conducted in a similar manner, arrives at the number 68·51, or 856·2.

5. *Bismuth.*—100 parts of the metal converted into nitrate, and decomposed by heat in a glass vessel, gave 111·275 of oxide, BiO_3, hence the atomic weight of bismuth is 212·86 (Lagerhjelm). Dumas, from a mean of seven experiments upon the quantity of silver required to precipitate the chlorine from a given weight of terchloride of bismuth, obtained 210·34, or 2629·2 as the number for this metal.

6. *Boron.*—According to Berzelius, 100 parts of borax lost

47·1 of water, and yielded 16·31 of soda, leaving for boracic acid (by difference) 36·59; and Davy found, by the direct combustion of boron, that 100 parts of boracic acid contain 32 of boron and 68 of oxygen. This would make the number for boron 10·9, or 136·2. But the methods which were employed are admitted by Berzelius not to be such as to warrant entire confidence in the accuracy of this number; and Deville, from his experiments upon the chloride and the bromide of boron, regards 11 as nearer the truth.

7. *Bromine.*—De Marignac found that 3·946 grammes of silver, when dissolved in nitric acid, required 4·353 grammes of bromide of potassium for its complete precipitation; and 15·00 of silver converted into nitrate gave 26·11 of bromide of silver: taking the equivalent of silver at 107·97, a mean of the experiments gives the equivalent of bromine as 79·97; and this result has been verified by Dumas by the decomposition of bromide of silver in a current of chlorine. It may without sensible error be taken as 80, or 1000.

8. *Cadmium.*—Stromeyer found that 114·352 parts of the oxide yielded 14·352 of oxygen; from which the equivalent of this metal is 55·74. Dumas found, as a mean of six experiments upon the quantity of silver required to precipitate the chlorine from a given weight of chloride of cadmium, the number 56·12 or 701·5; but the numbers obtained in the different experiments are not quite so concordant as usual.

9. *Calcium.*—Dumas, by the ignition of 100 parts of Iceland spar, obtained 56 parts of lime, which would make the equivalent of calcium exactly 20; and later experiments by the same chemist upon the quantity of silver required to precipitate a given weight of chloride of calcium, gave, as a mean of three experiments, 20·01. Erdmann and Marchand found it 20·03; De Marignac, by decomposition of a known weight of the chloride of calcium, estimated it at 20·105; and Berzelius, by the conversion of a known weight of pure lime into sulphate, found it to be 20·13. The number 20, or 250 may be safely adopted.

10. *Carbon.*—The determination of the equivalent of carbon formed the subject of a laborious series of researches by Dumas and Stas. They burned graphite, diamond, and charcoal in a current of pure oxygen with scrupulous care. 1·375 grammes of diamond gave 5·041 of carbonic acid; and the mean of their results, which agreed very closely with each other, fixed the equivalent of carbon at 6, or 75. Similar experiments by Erdmann and

Marchand gave them as a result, 6·007; and the results obtained by Liebig and Redtenbacher from the combustion of the oxalate, the acetate, the racemate, and the tartrate of silver, yielded 6·06, which coincides so nearly with that of Dumas, that these chemists themselves have adopted the number 6.

11. *Chlorine.*—Numerous careful experiments have been made with a view to determine the equivalent of chlorine. De Marignac found that 100 parts of chlorate of potash, when decomposed by heat, left 60·839 of chloride of potassium; and 22·032 of pure silver required 15·216 of chloride of potassium for its complete precipitation. 14·427 of chloride of potassium gave 27·749 of chloride of silver. Berzelius calculates from these results that the equivalent of chlorine is 35·46; and this coincides exactly with the recent elaborate experiments of Stas.

Maumené, by heating chloride of silver in a current of hydrogen, found that 100 parts of silver were united with 32·856 of chlorine. The same chemist obtained from 100 parts of chlorate of potash 60·791 of chloride of potassium: and from 100 parts of chloride of potassium, he obtained by precipitation 192·75 of chloride of silver. These experiments furnish data from which the equivalents of potassium and of silver may be determined, as well as that of chlorine, in the manner following:—

The composition of chlorate of potash is represented by the formula KO,ClO_5; when heated it gives off the whole of its 6 equivalents of oxygen. The equivalent of chloride of potassium therefore will be the quantity which is combined with 48 parts (or 6 equivalents) of oxygen. Now, taking Maumené's result that 39·209 parts of oxygen are combined in chlorate of potash with 60·791 of chloride of potassium, we have—

$$39{\cdot}209 : 48 :: 60{\cdot}791 : x \ (=74{\cdot}4208,\ 1\ \text{eq. of KCl}).$$

If 100 parts of chloride of potassium produce 192·75 of chloride of silver, 1 equivalent or 74·4208 of chloride of potassium will furnish 1 equivalent of chloride of silver. Thus—

$$100 : 192{\cdot}75 :: 74{\cdot}4208 : x \ (=143{\cdot}446,\ 1\ \text{eq. of AgCl});$$

and 132·856 of chloride of silver contain 32·856 of chlorine; consequently (1 atom of chloride of silver containing 1 atom of chlorine), we find the atomic weight of chlorine as follows:—

$$132{\cdot}856 : 32{\cdot}856 :: 143{\cdot}446 : x \ (=35{\cdot}476):$$

but the atomic weight of chloride of silver being	$=143\cdot446$
that of silver is found by deducting the equivalent of Cl	$=35\cdot476$
leaving the atomic weight of silver	$=107\cdot970$
and the atomic weight of chloride of potassium being	$=74\cdot4208$
deduct from it the atomic weight of chlorine	$=35\cdot476$
we obtain the atomic weight of potassium	$=38\cdot9448$

No material error can therefore arise if the atomic weight of

chlorine be taken as	$=35\cdot5$ or $443\cdot75$
that of silver as	$=108\cdot0$ or $1250\cdot0$
and that of potassium as	$=39\cdot0$ or $487\cdot5$.

Dumas has also checked these numbers by burning finely divided silver in a current of perfectly dry chlorine. He thus found that 108 parts of silver combined with 35·505 of chlorine as a mean of two experiments.

12. *Chromium.*—The combining number of chromium was determined by Berlin, by converting chromate of silver into the chloride; the number thus obtained was 26·347; and that deduced from the reduction of the chromic acid to the sesquioxide of chromium, in the same series of experiments, was 26·27, or 328·38. Péligot, from the analysis of the acetate, estimates it at between 26 and 26·8, but considers 26·24 as nearest the truth.

13. *Cobalt.*—Rothoff found that 269·2 parts of the protoxide of cobalt, when converted into protochloride by means of hydrochloric acid and precipitated by means of nitrate of silver, gave 1029·9 of chloride of silver: hence, if the cobalt be in the form of protoxide, the equivalent of cobalt is 29·49, or 368·65. Dumas, by similar means, obtained the number 29·54 as a mean of 5 experiments; but Schneider, by determining the relative amounts of carbon and cobalt contained in the oxalate, estimates the number of cobalt at 30. Further experiments upon this metal are desirable

14. *Copper.*—Berzelius obtained from 7·68075 grammes of oxide of copper, which were reduced in a current of hydrogen 6·13075 of metallic copper; hence the equivalent of the metal is 31·75, or 395·69. Erdmann and Marchand, by a similar method fixed it at 31·76.

15. *Fluorine.*—Berzelius found that 100 parts of fluor-spar when heated with an excess of sulphuric acid, yielded 175 of sulphate of lime. Louyet, on repeating this experiment, obtained 174·361 parts of sulphate of lime. The equivalent of fluorine de

duced from this latter result is 19, or 237·5. (*See* p. 150.) And these results have been confirmed by Dumas, who made similar experiments upon the fluorides of calcium, potassium, and sodium.

16. *Glucinum.*—Awdejew found that 100 parts of the chloride of this metal contained 88·42 of chlorine; hence, if the chloride be represented at Gl_2Cl_3, the combining number of the metal will be 6·97; but if the chloride be regarded as *Gl*Cl, the atomic weight of the metal is 4·65, or 58·1.

17. *Gold.*—Berzelius, by reducing the double chloride of gold and potassium in a current of hydrogen, determined the combining number of this metal at 196·66, or 2458·33. By an earlier series of experiments, he found that 142·9 of metallic mercury precipitated 93·55 of gold from the terchloride; 3 atoms of mercury causing the precipitation of 1 atom of gold: and assuming the atomic weight of mercury to be 100, this would make the number for gold 196·44.

18. *Hydrogen.*—The equivalent of hydrogen was determined with great care by Dumas, by the method already described at p. 46. He ascertained, as a mean of nineteen experiments, that 8 parts of oxygen combined with 1·0012 of hydrogen to form water; the lowest quantity which these experiments gave being 0·9984, the highest 1·0045. The quantity of water collected in each of these experiments was considerable, varying from 230 to 1100 grains. Erdmann and Marchand repeated these experiments with similar results. Berzelius and Dulong concluded, from researches performed long previously upon a similar principle, though on a smaller scale, that the quantity of hydrogen united with 8 parts of oxygen was 0·9984, which coincides with the lowest number obtained by Dumas. It is obvious that no appreciable error can be committed by assuming hydrogen to possess an equivalent of 1, that of oxygen being 8, or 12·5, if oxygen be taken at 100.

19. *Iodine.*—De Marignac determined the number for iodine by a process analogous to that which he employed for chlorine. The equivalent of iodide of potassium he fixed at 165·951; deducting from this 38·95, Maumené's number for potassium, we obtain 127 as the combining number of iodine, or 1587·5. Dumas, by two experiments upon iodide of silver, which he converted into chloride by heating it in a current of dry chlorine, obtained the same result.

20. *Iridium.*—Berzelius deduced the number for iridium from an analysis of the chloride of iridium and potassium ($KCl,IrCl_2$); he fixed it at 98·56, or 1232·08, which is identical with the number obtained for platinum.

21. *Iron.*—Berzelius found that 1·586 grammes of pure iron converted first into nitrate, and then into sesquioxide by ignition, gave 2·265 of sesquioxide; and Svanberg and Norlin, by reducing sesquioxide of iron in a current of hydrogen, obtained from 35·783 of sesquioxide, 25·059 of metallic iron; making the atomic weight of iron 28·04, or 350·5. Erdmann and Marchand, by the method last named, fixed the equivalent at 28·001, and Maumené has also arrived at a similar result by the oxidation of iron by aqua regia, and precipitating the oxide by means of ammonia. Still more recently, Dumas has obtained the same number by decomposing the chloride of iron by means of nitrate of silver—the mean of his four experiments being 28·07.

22. *Lead.*—21·9425 grammes of oxide of lead were reduced by Berzelius in a current of hydrogen, and gave 20·3695 of metallic lead; as a mean of five experiments, he determined the equivalent of the metal at 103·57 or 1294·645. This result has been confirmed by De Marignac, who obtained, by the precipitation of 5 grammes of chloride of lead 3·8835 of chloride of silver; and Dumas, by similar experiments, found the number for lead to be 103·55, whilst Stas estimates it at 103·456.

23. *Lithium.*—The number obtained by Berzelius for this metal, by neutralizing fused carbonate of lithia with sulphuric acid, is probably inaccurate, as the carbonate of lithia has subsequently been found to lose a little of its acid when melted. Mallet estimates the atomic weight of lithia at 6·97, or 87·1.

24. *Magnesium.*—Berzelius found that 100 parts of magnesia, dissolved in pure sulphuric acid and ignited, gave 293·985 of sulphate of magnesia; hence the equivalent of magnesium would be 12·65; but this result is probably a little too high.

Scheerer, by ascertaining the quantity of sulphate of baryta produced by a given weight of sulphate of magnesia, determined the number for magnesium at 12·11. Svanberg and Nordenfeldt, by the decomposition of the oxalate of magnesia ($2MgO,C_4O_6$, $4\,HO$) by heat, estimated it at 12·35; and by converting a known weight of magnesia into sulphate, found it to be 12·37; and Marchand and Scheerer, by ignition of the native carbonate, assigned to it the number 12·02. Dumas found extraordinary difficulty in procuring chloride of magnesium quite free from magnesia. The mean of 11 experiments upon the precipitation of the chloride by nitrate of silver gave 12·3 as the combining number of magnesium. The mean of these results is 12·16, or 152.

25. *Manganese.*—4·20775 of chloride of manganese gave Ber-

zelius 9·575 of chloride of silver; the equivalent of the metal, from a mean of two such experiments, is 27·57, or 344·684. Dumas, as a mean of five experiments conducted in a similar manner, obtained the number 27·48.

26. *Mercury*.—Erdmann and Marchand obtained from 118·3938 grammes of red oxide of mercury 109·6308 of mercury; a mean of five experiments gives 100·1, or 1251·29 as the equivalent of the metal. It may be safely estimated at 100.

27. *Molybdenum*.—Berzelius regarded the number 47·96, given by himself for this metal, only as an approximation. Svanberg and Struve, from an extensive series of experiments, considered that the most accurate results were obtained by roasting the bisulphide of molybdenum in air, and they conclude that 100 parts of the bisulphide yield 89·732 of molybdic acid; hence, if the equivalent of sulphur be taken at 16, that of molybdenum will be 46·06. Berlin, from the quantity of molybdic acid left by the salt (H_4NO, $2\,MoO_3 + H_4NO$, $3\,MoO_3 + 3HO$), found the number for the metal (from a mean of four experiments) to be 45·98. Dumas, however, by reducing crystallized molybdic acid in a current of hydrogen, found, as a mean of 5 concordant experiments, 48, or 600, as the number for this metal.

28. *Nickel*.—Rothoff converted 188 parts of oxide of nickel into chloride, and obtained from it 718·2 of chloride of silver; the number for nickel hence deduced is 29·54, or 369·333; and Dumas, as a mean of 5 experiments on the same plan, obtained the number 29·51; though Schneider, by the analysis of the oxalate, estimates it at 29. Here further experiments are therefore wanted.

29. *Nitrogen*.—De Marignac, by converting 200 grammes of silver into nitrate, obtained 314·894 of the salt; 14·110 of nitrate of silver required for precipitation 6·191 of chloride of potassium; 10·339 of silver converted into nitrate required 5·120 of chloride of ammonium for complete precipitation; the mean result, as calculated by Berzelius from several experiments performed in this manner, gives 14·004 as the number for nitrogen. Stas, by synthetic experiments upon nitrate of silver, fixed it at 14·041. Anderson, by the decomposition of nitrate of silver by heat, concluded that the atomic weight of nitrogen was 13·95; and Svanberg, from the analysis of nitrate of lead, obtained the same result: the number for nitrogen may therefore be taken as 14, or 175.

30. *Osmium*.—The atomic weight of this metal was calculated by Berzelius from the result obtained by heating the chloride of osmium and potassium ($KCl,OsCl_2$) in a current of hydrogen, 1·3165 grammes of the salt leaving 0·401 gramme of KCl and

0·535 grm. of osmium : hence the number for osmium was estimated at 99·4, or 1242·68, which agrees with the later researches of Dumas.

31. *Oxygen.*—The equivalent of oxygen is the standard to which all others are referred; it is found to be a multiple by 8 of that of hydrogen.

32. *Palladium.*—The number for this metal rests upon the authority of Berzelius, who found, by reducing the chloride of potassium and palladium (KCl,PdCl) in a current of hydrogen, that 2·606 grammes of the salt gave 0·563 gramme of chlorine, 0·851 of palladium, and 1·192 KCl: hence the atomic weight of palladium is 53·24 or 665·47.

33. *Phosphorus.*—According to Pelouze, a solution of 100 parts of silver in nitric acid is required to precipitate the chlorine from 42·74 of terchloride of phosphorus; the atomic weight, therefore, would be 32·02 or 400·3. Berzelius, from the silver reduced from sulphate of silver by a known weight of phosphorus, estimated the number for phosphorus at 31·36; and Schrötter concludes—from a mean of ten experiments, in which phosphorus was burned in a current of dry air, and thus converted into phosphoric acid—that the true atomic weight is 31, or 387·5; a result confirmed by careful experiments upon the terchloride by Dumas, who found it to be 31·03.

34. *Platinum.*—Berzelius found that 6·981 grammes of the double chloride of platinum and potassium, when reduced in a current of hydrogen, gave 4·957 of a mixture of platinum and chloride of potassium; 2·822 of this was platinum: hence the number for platinum is 98·56, or 1232·08.

35. *Potassium.*—De Marignac's experiments on the chlorate of potash (related when speaking of the atomic weight of chlorine) gave the number for potassium, 39·1; those of Maumené, 38·95; those of Pelouze, 39·14; and those of Stas, 39·13. It may therefore be taken as 39, or 487·5.

36. *Rhodium.*—3·146 grammes of the chloride of rhodium and potassium (KCl,Ro_2Cl_3) when heated in a current of hydrogen, were found by Berzelius to furnish 0·912 gramme of rhodium, and 0·515 gramme of chloride of potassium; whence he calculates the equivalent of the metal at 52·16, or 651·96.

37. *Selenium.*—100 parts of selenium, when heated in a current of chlorine, yield exactly 279 of bichloride of selenium, according to Berzelius, which would make the equivalent 39·66, or 495·3; but the method employed is not perfectly trustworthy. Dumas, by modifying the method of proceeding, obtained, as a mean of seven experiments, 39·73.

38. *Silicon.*—Berzelius found that 100 parts of silicon, when

oxidized, yielded 208 parts of silica, which if taken as SiO_2 would give an atomic weight of 14·81; this appears to be too high. Pelouze states that a solution of 3·685 parts of silver in nitric acid precipitated 1·454 of chloride of silicon, whence the number would be 14·24; and Dumas, by a mean of two experiments conducted on the same principle, obtained the number 14·01, or 175·1.

39. *Silver.*—The combining number of this metal has been repeatedly determined with very great care, as it forms a fundamental datum in these inquiries. De Marignac, by precipitation of a known weight of silver from its solution in nitric acid, as chloride, estimates the equivalent as 107·97; and the experiments of Pelouze and of Maumené agree almost exactly with this result. Dumas has also confirmed this result by burning finely divided silver in a current of chlorine gas; and the number deduced by Stas, from his experiments, was 107·945. 108, or 1350, may therefore be taken as the atomic weight of silver.

40. *Sodium.*—Berzelius found that 100 parts of chloride of sodium gave by precipitation 244·6 of chloride of silver; the equivalent of sodium would therefore be 23·17. Pelouze found, as a mean of three experiments, that 100 parts of silver required for precipitation 54·144 of chloride of sodium, whence the equivalent of sodium would be 22·97. Dumas, as a mean of seven experiments of a similar kind, obtained the number 23·01; and Stas found it to be 23·05. It may be taken as 23, or 287·5.

41. *Strontium.*—The number for this metal was also obtained by a similar method, viz., by ascertaining the proportion of silver which a given weight of chloride of strontium required for precipitation. Stromeyer thus fixed the number at 43·67; De Marignac at 43·77; Pelouze at 43·84; and Dumas, from a numerous series of experiments, at 43·74, or 546·7.

42. *Sulphur.*—The equivalent of sulphur was estimated by Berzelius from the weight of sulphate of lead formed by oxidizing a known weight of lead with nitric acid, and heating it with an excess of sulphuric acid till the weight ceased to alter. As a mean of three experiments, 100 parts of lead yielded 146·45 of sulphate of lead; hence the equivalent of sulphur would be 16·064; this result was confirmed by converting chloride of silver into sulphide in a current of dry sulphuretted hydrogen. Erdmann and Marchand, by distilling cinnabar with copper turnings, obtained from 100 parts of cinnabar 86·213 of mercury as a mean of two experiments. This would make the equivalent of sulphur exactly 16, or 200,—a result which agrees with those of Dumas, who converted a given weight of silver into sulphide, by heating the metal

in the vapour of sulphur. As a mean of five such experiments, he obtained the number 16·01, while Stas found it to be 16·0371.

43. *Tellurium.*—1·5715 gramme of tellurium when oxidized by nitric acid and heated till the excess of nitric acid was expelled, left a residue of TeO_2, which Berzelius found to weigh 1·9365 gramme; hence the number for tellurium would be 64·15. But Dumas, from experiments not hitherto published in detail, regards it as 64·5, or 806·25.

44. *Tin.*—100 parts of tin, when oxidized by nitric acid and ignited, were found by Berzelius to yield 127·2 parts of peroxide; from which the number for tin would be 58·82. Mulder states that he obtained from 100 parts of this metal 127·56 of peroxide of tin, which would give the number 58·05. Dumas, on repeating this experiment, obtained the number 59·03 for the metal, and this result was confirmed by experiments on the quantity of silver required for the precipitation of a known weight of bichloride of tin. The atomic weight of tin may therefore be taken at 59, or 737·5.

45. *Titanium.*—The number for this metal rests upon the analysis of its bichloride. Rose found, as a mean of four experiments, that 100 parts of the bichloride contained 74·46 of chlorine, which would give 24·12 as the atomic weight of titanium. Later experiments by Isidore Pierre, seem to fix it at 25·17, or 314·7.

46. *Tungsten.*—The number 94·64 given by Berzelius was only an approximation to the true one for this metal. Schneider, on repeating the experiment of reducing tungstic acid in a current of hydrogen, found that 100 parts of the acid yielded 79·316 of the metal, and on oxidizing metallic tungsten, and reconverting it into tungstic acid, he found 79·327 parts of metal furnished 100 of acid; the atomic weight of tungsten from the mean of these results would be 92·06. Marchand, by similar experiments, fixed it at 92·05, a result completely confirmed by Dumas. It may be taken as 92, or 1150.

47. *Uranium.*—Some doubt exists as to the exact combining number of this metal. Wertheim estimates it at 740·51, from the double acetate of soda and uranium; and Ebelmen at 742·87, from the oxalate. Ebelmen's number would give the number on the hydrogen scale as 59·43; but Péligot's estimate of 60, or 750 is usually adopted.

48. *Vanadium.*—The atomic weight of this metal was determined by heating vanadic acid in a current of hydrogen. It was thus reduced to the protoxide. Berzelius found as a mean of four experiments, that 100 parts of the acid lost thus 20·927 of oxygen. Hence the atomic weight of the metal is calculated at 68·55, or 856·89.

49. *Zinc.*—Favre, from the analysis of the oxalate of zinc, and from the determination of the quantity of hydrogen which a given weight of zinc liberates during its solution in hydrochloric acid, fixed this equivalent at 33·0; and Jacquelain, by the decomposition of the nitrate and of the sulphate of zinc by heat, obtained the number 33·12. The original number given by Berzelius for this metal was 32·25. Subsequently, A. Erdmann prepared a pure oxide of zinc, mixed it with pure charcoal obtained from sugar, and distilled the zinc in a current of hydrogen; he then oxidized the metal by nitric acid, and converted it into oxide by ignition. The combining number of zinc, taking a mean of four experiments conducted in this manner, was 32·52, or 406·59. Pelouze obtained the same number from the analysis of the lactate of zinc.

50. *Zirconium.*—As a mean of six experiments, Berzelius found that 100 parts of sulphuric acid, (SO_3), required 75·853 of zirconia, in order to form the sulphate of the earth. Fluoride of zirconium forms with fluoride of potassium two compounds: in one the fluorine is combined with zirconium and potassium in equal quantity; in the other the ratio of fluorine to the zirconium is as 3, if that with potassium is 2: hence Berzelius considers that zirconia contains Zr_2O_3, and the combining number of the metal is 33·59, or 419·73; but De Marignac has shown (see *note* p. 484) that zirconia is more probably ZrO, in which case the number would be 22·4.

(895) *Table of Combining Numbers.*—We may here sum up the foregoing results, by stating that the following numbers may be taken, for the purpose of calculation, as representing the atomic weights of the elementary bodies on the hydrogen scale. They differ but very slightly from the numbers given at page 18 of Part I:—

Aluminum	13·7	Gold	196·6	Potassium	39·0
Antimony	122·0	Hydrogen	1·0	Rhodium	53·2
Arsenic	75·0	Iodine	127·0	Ruthenium	52·0
Barium	68·5	Iridium	98·6	Selenium	39·7
Bismuth	210·3	Iron	28·0	Silicon	14·0
Boron	10·9	Lanthanum	46·0	Silver	108·0
Bromine	80·0	Lead	103·6	Sodium	23·0
Cadmium	56·0	Lithium	7·0	Strontium	43·8
Calcium	20·0	Magnesium	12·16	Sulphur	16·0
Carbon	6·0	Manganese	27·5	Tantalum	68·8
Cerium	46·0	Mercury	100·0	Tellurium	64·5
Chlorine	35·5	Molybdenum	48·0	Thorinum	59·5
Chromium	26·3	Nickel	29·5	Tin	59·0
Cobalt	29·5	Nitrogen	14·0	Titanium	25·0
Columbium	48·8	Osmium	99·4	Tungsten	92·0
Copper	31·7	Oxygen	8·0	Uranium	60·0
Didymium	48·0	Palladium	53·2	Vanadium	68·5
Fluorine	19·0	Phosphorus	31·0	Zinc	32·6
Glucinum	4·7	Platinum	98·6	Zirconium	33·6

(895 *a*) *On the Numerical Relations of the Proportional Numbers of the Elements.*—Several years ago Prout started the idea that the numbers which represent the combining proportions of the different elementary bodies were multiples by whole numbers of the combining proportion of hydrogen; and he attributed the various cases of apparent departure from this proposition to inaccuracy in the experimental determinations of the combining proportion of the exceptional bodies. Since that period an increased degree of precision has been attained in experiments of this nature, and many of the apparent exceptions to Prout's idea have been removed.

Independently of the importance of accurate determinations of these numbers for the purposes of chemical analysis, and for the tracing out of quantitative relations between the chemical equivalents and certain physical properties, such as the density and specific heat of the simple and compound bodies, the verification or disproof of Prout's hypothesis acquires a high interest from its connexion with the nature of the elementary bodies themselves; for if the combining proportions of all the elements be multiples by whole numbers of the combining proportion of hydrogen, it is not absolutely impossible that the various bodies at present regarded as elementary, may in reality be *compounds* of a single primordial substance condensed in different degrees in the various so-called elements.

If experiment justifies the hypothesis of Prout, it would be possible that the three following propositions were true:—

a. Similar quantities of this one elementary principle might, by variety in the mode of their arrangement, form bodies (at present regarded as elementary), or radicles of equal atomic weight, but endowed with distinct properties.

b. A radicle intermediate in properties, and in its combining number between two other radicles of the same group, might be produced by the union of half a molecule of the two extreme radicles.

c. And, finally, the supposed constitution of these radicles (or bodies at present regarded as simple) might be assimilated to the compound radicles of organic chemistry of known constitution. There would be, however, this important distinction between the radicles of mineral chemistry and those of organic origin; viz., that the radicles of inorganic chemistry possess a stability infinitely greater than those of the organic creation—a stability, indeed, of such an order, that the present resources of analytical chemistry are insufficient to effect their decomposition.

The probability, on the other hand, of such views would obviously be negatived if the elements exhibited no such multiple relation in their equivalents.

Certain remarkable relations which exist between many of these numbers have been pointed out by various chemists. The whole subject of atomic weights has recently been subjected to a careful revision by Dumas (*Ann. de Chimie*, III. lv. 129). As the result of his investigations and calculations, Dumas concludes that, in a modified sense, Prout's law is true; and he considers that the elementary bodies, the atomic weights of which he regards as accurately known, may be arranged in three groups;* viz.,

1. Bodies which are represented by multiples of a whole number of hydrogen.

2. Multiples by the number 0·5 of that of hydrogen.

3. Multiples by 0·25 of that of hydrogen.

1. Bodies which are multiples by a whole number of the equivalent of hydrogen:—

Hydrogen	1	Molybdenum	48
Carbon	6	Cadmium	56
Oxygen	8	Tin	59
Nitrogen	14	Arsenic	75
Silicon	14	Bromine	80
Sulphur	16	Tungsten	92
Fluorine	19	Mercury	100
Calcium	20	Silver	108
Sodium	23	Antimony	122
Iron	28	Iodine	127
Phosphorus	31	Bismuth	210

2. Multiples by 0·5 of the equivalent of hydrogen.

Manganese	27·5	Tellurium	64·5
Cobalt	29·5	Barium	68·5
Nickel	29·5	Osmium	99·5
Chlorine	35·5	Lead	103·5

3. Multiples by 0·25 of the equivalent of hydrogen.

Aluminum	13·75	Selenium	39·75
Copper	31·75	Strontium	43·75
Zinc	32·75		

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* Stas, however, arrives at an opposite conclusion. He has just published a long and most laborious series of researches, which it appears almost impossible to surpass in precision. In this memoir he gives the following numbers for some of the most important elements:—

Oxygen	8	Sodium	23·05
Silver	107·945	Nitrogen	14·041
Chlorine	35·46	Sulphur	16·0371
Potassium	39·13	Lead	103·456

These results have been obtained in each case by several different processes;

The relations exhibited between the members of many of these bodies which are chemically allied are often very remarkable.

1. Thus, it has been observed that, in several instances where two elements are in close chemical relation to each other, they have atomic weights which are identical; this happens, for example, with the following pairs of bodies:—

Cobalt and nickel	29·5
Lanthanum and cerium	46·0
Rhodium and ruthenium	52·1
Platinum and iridium	98·5

2. In other cases, the ratio of the atomic weights is as 1 to 2; for instance:—

Oxygen .	= 8	Sulphur .	= 16
Aluminum	= 13·75	Manganese	= 27·5

3. It has also been stated that, where three elements belong to the same natural group, the atomic weight of the intermediate element is frequently equal to the mean of those of the two extremes. This is true in the case of

$$\begin{array}{l} \text{Lithium .} = 7 \\ \text{Sodium .} = 23 \\ \text{Potassium} = 39 \end{array} \quad ; \quad \frac{7+39}{2} = 23;$$

the number for sodium being the arithmetic mean of those for lithium and potassium: but this is the only case in which this relation is rigidly in accordance with the experimental numbers. Several groups agree very nearly with such a supposition, but the

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and the differences between the various numbers thus arrived at for the same body are in all cases much smaller than the difference between the mean result and the whole number required by Prout's law. These numbers were obtained by operating with balances of unusual delicacy; and upon quantities much larger than is customary in researches of this kind,—the quantities amounting in some cases to nearly a pound weight of the materials.

The numbers thus obtained do not differ from those of Dumas, or indeed from those in general use, sufficiently to affect any calculations of analyses founded upon them; but from the variety of methods employed, and the extraordinary degree of care and precision with which the experiments were made, the results are of the highest value in relation to the hypothesis of Prout.

M. Stas concludes his memoir with these words:—

'So long as we adhere to the results of experiment for the establishment of the laws by which matter is governed, we ought to consider the law of Prout as a pure illusion, and should regard the indecomposable substances of our globe as distinct bodies, having no simple relations between their atomic weights. The undeniable analogy in properties which is observed in certain of the elements must be sought for in other causes than those derivable from the relations in weight of their acting masses.'

We cannot too jealously watch any twisting of experimental data to suit our theories; and those who are familiar with the speculations on the numerical relations of the atomic weights, cannot but feel that the severe method of induction from facts has in this case been more than usually departed from by the followers of a sciencewhich is pre-eminently one of experiment.

divergence is, notwithstanding, too great to admit of being attributed to errors of experiment. For example:—

$$\begin{array}{lll} \text{Calcium} = 20 & & 20+68{\cdot}5 \\ \text{Strontium} = 43{\cdot}75 & ; & \overline{} = 44{\cdot}25 \\ \text{Barium} = 68{\cdot}5 & & 2 \end{array}$$

$$\begin{array}{lll} \text{Sulphur} = 16 & & 16+64{\cdot}5 \\ \text{Selenium} = 39{\cdot}75 & ; & \overline{} = 40{\cdot}25 \\ \text{Tellurium} = 64{\cdot}5 & & 2 \end{array}$$

In both these groups, the difference between the experimental and the calculated number of the intermediate element amounts to 0·5; and it is probable that this difference is physically true.

In cases like the lithium and calcium groups, it has been suggested, both by Pettenkofer and by Dumas, that the relation between the different members of the group may be analogous to that observed in bodies of organic origin which belong to the same homologous series (914). The reader who is desirous of pursuing this speculation will find it ably and clearly discussed by Dumas in his paper already cited (*Ann. de Chimie,* III. lv.).

(896) *Gerhardt's Notation.*—Gerhardt, starting with the assumption that the equivalents of all compound bodies yield two volumes of vapour, has been induced to modify some of these numbers; and this proposal has within the last few years been warmly discussed, and adopted by some chemists of eminence. On the proposal of Gerhardt, the numbers for oxygen, carbon, sulphur, selenium, and tellurium are double of those commonly made use of; these numbers being as follows:—

Oxygen $= 16 = O$	Selenium $= 79{\cdot}5 = Se$
Carbon $= 12 = C$	Tellurium $= 129{\cdot}0 = Te$;
Sulphur $= 32 = S$	

the other numbers remaining unaltered. In the inorganic division of the science, comparatively little advantage is gained by this change; but in many instances, where organic compounds are considered, the method leads to a considerable simplification of the formulæ employed. A few formulæ are subjoined for the purpose of contrasting them with those in ordinary use:—

Compounds.	Ordinary Formulæ.	Gerhardt's Formulæ.
Water	HO	H_2O.
Potash	KO	K_2O.
Hydrate of Potash	KO,HO	KHO.
Oxide of Silver	AgO	Ag_2O.
Hydrochloric Acid	HCl	HCl.
Chloride of Potassium	KCl	KCl.
Ammonia	H_3N	H_3N.
Protoxide of Nitrogen	NO	N_2O.
Binoxide of Nitrogen	NO_2	NO.

Compounds.	Ordinary Formulæ.	Gerhardt's Formulæ.
Hydrated Nitric Acid	HO,NO_5	NO_6H.
Nitrate of Potash	KO,NO_5	NO_3K.
Carbonic Acid (Anhydride)	CO_2	CO_2.
Carbonate of Potash	KO,CO_2	CO_3K_2.
Bicarbonate of Potash	$HO,KO,2\,CO_2$	CO_3KH.
Hydrated Sulphuric Acid	HO,SO_3	SO_4H_2.
Sulphate of Potash	KO,SO_3	SO_4K_2.
Bisulphate of Potash	$KO,HO,2\,SO_3$.	SO_4KH.
Hydrated Tribasic Phosphoric Acid	$3\,HO,PO_5$	PO_4H_3.
Tribasic Phosphate of Soda	$3\,NaO,PO_5$	PO_4Na_3.
Ordinary Phosphate of Soda	$2\,NaO,HO,PO_5$	PO_4Na_2H.
Pyrophosphate of Soda	$2\,NaO,PO_5$	$P_2O_7Na_4$.
Metaphosphate of Soda	NaO,PO_5	PO_3Na.
Alumina	Al_2O_3	Al_4O_3.
Alum (dried)	$\left\{ \begin{matrix} KO,SO_3+Al_2O_3 \\ 3\,SO_3 \end{matrix} \right\}$	$K_2Al_4\,4\,SO_4$.
Oxide of Chromium	Cr_2O_3	Cr_4O_3.
Chromic Acid	CrO_3	Cr_2O_3.
Chromate of Potash	KO,CrO_3	$K_2Cr_2O_4$.
Bichromate of Potash	$KO,2\,CrO_3$	$K_2Cr_2O_4+Cr_2O_3$.
Grey Oxide of Mercury	Hg_2O	Hg_4O.
Calomel	Hg_2Cl	Hg_2Cl.
Red Oxide of Mercury	HgO	Hg_2O.
Corrosive Sublimate	$HgCl$	$HgCl$.
Hydrated Acetic Acid	$HO,C_4H_3O_3$	$C_2H_4O_2$.
Acetate of Potash	$KO,C_4H_3O_3$	$C_2H_3KO_2$.
Acetic Anhydride	$(C_4H_3O_3)_2$	$C_4H_6O_3$ or $\left\{ \begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix} \right\} O$.
Alcohol	HO,C_4H_5O	C_2H_6O.

These illustrations of Gerhardt's system are sufficient to show that in certain cases it admits of being happily applied to compounds of inorganic origin, as well as to the more complex bodies derived from the department of organic chemistry. The acid sulphates and carbonates are thus assimilated to the normal sulphates and carbonates, and it will be observed that the dibasic nature of the acid in both these families of salts is a necessary consequence of the constitution of its molecule, the smallest particle of which is represented in the case of oil of vitriol (SO_4H_2), as containing *two* atoms of hydrogen, both of which admit of displacement by an atom of a metal (such as potassium or copper) which corresponds in basic power to hydrogen. In other instances, as in the pyrophosphates and the compounds of chromium, the formulæ of Gerhardt are more complicated than those in ordinary use.

The notation in common use has, however, many advantages over that proposed by Gerhardt:—1. The ordinary system is known to every one who has made the science of chemistry his study.*

* The confusion introduced by the new notation would be lessened if the advocates of the new views would agree to indicate the double atom of oxygen, carbon, or sulphur, by the plan of Berzelius, who distinguished certain

—2. All the memoirs, with the exception of a few in later years, are written in accordance with this system, and a change of notation would at once render these memoirs less easily accessible and intelligible.—3. The new notation is not in harmony with the language of Chemistry; NO, for example, would be called *binoxide* of nitrogen, but written as a protoxide.—4. The present system of notation is capable of expressing all the later theories with perfect precision, while it is applicable to the older views; but the new notation is not applicable to many of the older views. By the ordinary notation, nitrate of potash, for instance, may be represented either as a compound of potash and nitric acid (KO, NO_5), or as a combination of potassium with nitrion (K, NO_6), or as an aggregation of particles without indicating any specific mode of combination (KNO_6); whereas, in the new notation, unless its principle is abandoned by doubling the formulæ, it is impossible that (KNO_3) should be represented as formed of potash and nitric acid. It would, therefore, be a retrograde step thus to exclude from our notation the power of indicating the constitution of a large class of compounds upon a view which has long been more or less prevalent.—5. Any extensive change of nomenclature or of notation, while the truth of the theory upon which it rests is still under discussion, cannot but lead to serious inconvenience. If such a practice were admitted, every new theory would be privileged to introduce a new language, which, in a continually progressive science like Chemistry, would soon give way to an equally transitory successor. Chemistry, it must be remembered, is not merely a science: it is also an art, which has introduced its nomenclature and its notation into our manufactories, and, in some measure, even into daily life; it is therefore specially necessary to beware of needless innovation in its terms and symbols. Any system of notation, it must also be borne in mind, is a mere artificial contrivance to represent to the mind certain changes or certain hypotheses; and to argue for a system of notation as though it were anything more, as has sometimes been done, shows a want of true appreciation of its meaning.

The question to be considered is not simply, What is in the abstract the best mode of notation, but, What, considering all the circumstances of the science, possesses the greatest advantage. That system of notation which is consistent with itself, and which lends itself most completely to the expression of the various

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double atoms by drawing a line through the letter. The same object might be attained by writing the new symbols in Italic capitals, as in the foregoing Table.

theories and aspects of the science which have been maintaine
or may be maintained, is therefore, philosophically speaking, tl
best. And such grounds, it appears to me, exist for continuii
to use the system hitherto generally adopted.

This question of notation, it must be observed, is entire
independent of Gerhardt's theory of the atomic constitution
the elements to which he proposes to apply it. Even those wl
admit the truth of his hypothesis may still express the mol
cular constitution of compounds, as he did himself in his *Trai*
by the ordinary mode of notation.

INDEX TO PART II.

END OF PART II.

ERRATA IN PART II.

Page 24, 17 lines from bottom, for *gases*, read *gas*.
,, 63, 10 ,, ,, ,, $C_{18}H_{24}O_{22}$, read $C_{128}H_{4}O_{22}$.
,, 75, 21 ,, ,, ,, 9, read 12.
,, 97, 15 ,, top, for 2 HO,NO_5, read 2 (HO,NO_5).
,, 126, 23 ,, ,, ,, *Comb. Vol.* 2, read *Comb. Vol.* 3.
,, 159, 8 lines below table, after 1·38 dele 9.
,, 175, 3 ,, from top, for 148 read 48.
,, 206, 11 ,, ,, ,, 2 NaO, HO, read NaO, 2 HO.
,, 216, 19 ,, ,, bottom, for PHO_3, read PHO_4.
,, 220, 17 ,, ,, top, for 2 Si + 3 KF, read Si + 3 KF.
,, 251, last line (in some copies) for C_2H, read C_2H_4.
,, 318, 14 lines from bottom, at end of line, dele *be*.
,, 357, 2 ,, ,, transpose the words *acid* and *potash*.
,, 391, 17 ,, ,, for SiO, read SiO_2.
,, 395, 2 ,, top, the formula should be [$KO, 2\,SiO_2 + 2\,(CaO, 2\,SiO_2) + Al_2O_3, 6\,SiO_2$].
,, ,, next line, the formula should be ($KO, 2\,SiO_2 + CaO, 2\,SiO_2$).
,, 400, 14 lines from top, for ($3\,PbO, 2\,SiO_3$), read 3 ($PbO, 2\,SiO_3$).
,, 448, 12 ,, bottom, for 48·78, read 51·22.
,, 450, 6 ,, ,, for H (KCa) F, read *x* (KCa) F.
,, 462, 10 ,, top, for 63, read 134.
,, 510, 13 ,, bottom, for 5 Aq, read 3 Aq.
,, 528, last line but one of text, insert *for* before *castings*.
,, 544, 8 lines from top, for 8 and 4, read 10 and 5.
,, 563, 20 ,, bottom, for *hydrochloric*, read *hydrofluoric*.
,, 569, 8 ,, top, for *or*, read *of*.
,, 605, 14 ,, ,, ,, *blue* read *yellow*.
,, 608, 2 ,, bottom, for *anhydrides*, read *anhydride*.
,, 609, 2 ,, ,, ,, *needles*, read *thin brilliant plates*.
,, 610, 20 ,, top, for *exert an alkaline reaction on reddened litmus*, read *colour litmus of a wine red*.
,, 611, 3 ,, ,, for $H_4NO, 2\,HO, 3\,W_2O_6$, read, $H_4NO, 3\,HO, 3\,W_2O_6$.
,, 620, 18 ,, ,, ,, 7, read 9.
,, 624, in the equation for 6 CO, read 3 CO + 3 CO_2.
,, 633, 15 lines from top, for 1848, read 1858.
,, 645, 3 ,, ,, dele 6 Aq.
,, 677, last line, before *nitrate* insert *chlorate, and* 8 *parts of*.
,, 701, last line but two, for 4·666, read 6·466.
,, 702, 4 lines from bottom, for $NO_5 + HO$, read $NO_5 + 2HO$.
,, 703, 2 ,, top, for *white*, read *yellow*.
,, 752, 4 ,, bottom of text, for 222, read 223.
,, 767, 12 ,, ,, for *solution of osmic acid*, read *crystals of osmite of potash*.

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